



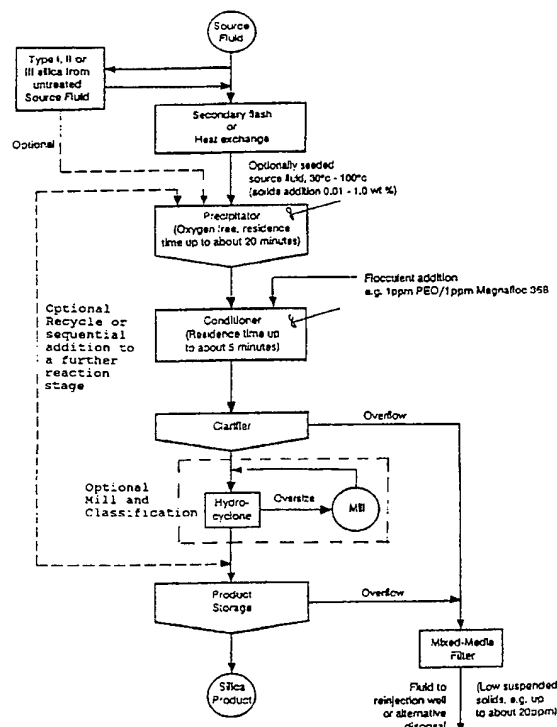
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C01B 33/12, D21H 17/68		A1	(11) International Publication Number: WO 94/18121
			(43) International Publication Date: 18 August 1994 (18.08.94)
(21) International Application Number: PCT/NZ94/00004		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 28 January 1994 (28.01.94)			
(30) Priority Data: 245823 1 February 1993 (01.02.93) NZ 247366 8 April 1993 (08.04.93) NZ			
(71) Applicants (for all designated States except US): TASMAN PULP & PAPER CO. LIMITED [NZ/NZ]; Shortland Street, Auckland (NZ). GEOCHEMISTRY RESEARCH LIMITED [NZ/NZ]; 102 Messines Road, Karori, Wellington (NZ).		Published With international search report.	
(72) Inventors; and			
(75) Inventors/Applicants (for US only): JOHNSTON, James, Howard [NZ/NZ]; 102 Messines Road, Karori, Wellington (NZ). HARPER, Ross, Thomas [NZ/NZ]; 87A Karori Road, Wellington (NZ).			
(74) Agents: BENNETT, Michael, R. et al.; A.J. Park & Son, 6th floor, Huddart Parker Building, Post Office Square, P.O. Box 949, Wellington 6015 (NZ).			

(54) Title: AMORPHOUS SILICA, ITS PREPARATION AND USES

(57) Abstract

A silica product preferably obtained from geothermal water, its uses (e.g. with paper) and preparation. It has a tertiary aggregate structure (preferably of Type I, II or III as defined in EP 0396242) with an average secondary particle dimensions up to about 30 nm., an oil absorption of greater than about 190 g.100g⁻¹ as measured by the spatula rubout method using linseed oil, a light scattering coefficient greater than about 280 m².kg⁻¹, a reflectance of greater than about 95 % at a wavelength of 557 nm. (using illuminant D65 and 10° viewing angle), and a BET surface area of greater than about 4m².g⁻¹.



Schematic Diagram of Continuous Process with Provision for Recycle

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

AMORPHOUS SILICA, ITS PREPARATION AND USES**TECHNICAL FIELD**

This invention is directed to a novel means of recovering amorphous silica from geothermal waters containing silicic acid and/or other siliceous values dissolved and/or dispersed therein. This invention extends further the novel process of recovering said amorphous silica from geothermal waters described in the New Zealand Patent No. 232170/228472 (EP 0396242), by using amorphous silica produced according to New Zealand Patent No. 232170/228472 as a precipitation agent or substrate onto which dissolved silica can be recovered from a process, either in a single step, a sequence of steps or a process involving continuous recycle. In this way the tertiary amorphous silica precipitation agent or substrate acts as a receptive surface, onto which the dissolved silica is recovered in a controlled manner, thereby enabling the secondary particle size, pore size, oil absorption, optical reflectivity and other properties of the amorphous silica product to be controlled. In particular, amorphous silica products with unexpectedly high oil absorption and light scattering properties can be produced.

This invention therefore further relates to the novel solid amorphous silica products produced by this novel recovery process.

It further relates to several unique uses for these novel products.

BACKGROUND ART

Moderate concentrations of silicic acid are present in hot, pressurized, aqueous, geothermal fluid as a result of the dissolution of silica-containing minerals from the rock material in contact with the geothermally heated water while it is still underground. This fluid may be discharged from normal surface manifestations or may be produced artificially, from wells drilled into suitable formations, which increase mass withdrawal, for whatever purpose. Usually, the purpose of drilling geothermal wells and producing the hot geothermal fluid is to provide an energy source for the production of electric power.

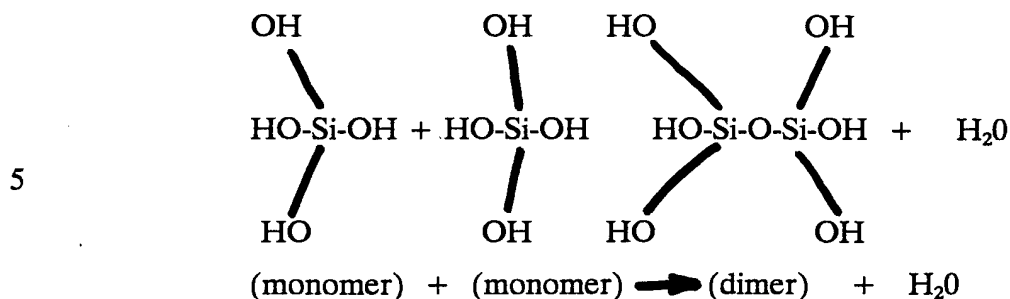
- 2 -

If silicic acid concentration in the water produced at the surface is sufficiently high, when the temperature or the pressure of the water is reduced, homogeneous nucleation, of the siliceous values in the produced water results in the formation of critical size nuclei, which rapidly grow to form primary particles
5 of silica. Spontaneous nucleation of the parent monomeric silicic acid species, and subsequent growth thereof by polymerization, forms polymeric primary silica particles which attain a physical dimension of about 1.5 nm.

Under slightly acidic to neutral conditions, this is best represented by the condensation reaction:

10

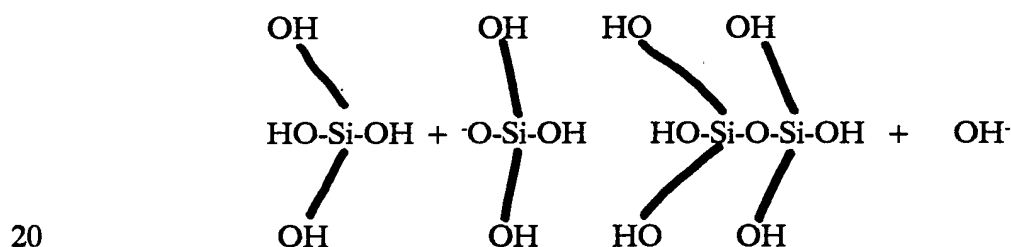
- 3 -



Under more alkaline conditions, e.g. pH > 7, dissociation of silicic acid to
 10 silicate ion becomes significant, according to the equation:



Polymerization under these conditions is considered to favour the following
 15 reaction:



Primary particles resulting from this type of reaction can be observed under
 a high power transmission electron microscope, as shown in Figure 1 of New
 Zealand Patent 232170/228472.

In this invention, the tertiary aggregate amorphous silica products are
 25 differentiated by structure into three (3) classifications, namely: Types I, II and
 III. The detailed structural features and characteristics of these three types of
 silica are described in New Zealand Patent No. 232170/228472.

The precipitated silicas described are classified as in New Zealand Patent
 No. 232170/228472 or EP 0396242 according to the structure they possess, viz
 30 **TYPE I:** Precipitated silica possessing primary, secondary and tertiary
 aggregate structure.

Primary silica particles are about 1.5 nm in size and secondary particulate

- 4 -

silica where discernible from overlap boundaries on electron micrographs, have random shapes approximately described in geometric terms by elongate ellipsoids.

Tertiary aggregate structure of this precipitated silica comprises the former particulates and is further characterized by the presence of secondary particulate "bridging silica" composed of primary silica particles. These serve to provide infill silica which completes the tertiary aggregate structure. There is uniformity with respect to secondary particulate and bridging silica size. These structural characteristics are illustrated in figs 1 - 3 of New Zealand Patent 232170/228472 and EP 0396242.

10 TYPE I precipitated silica satisfies the IUPAC classification for mesoporous material and is structurally consistent with G-type silica gels and pyrogenic "fume" silica produced from steam hydrolysis of silicon tetrachloride, e.g. Aerosils.

15 TYPE II: Precipitated silica possessing primary, secondary and tertiary aggregate structure.

Primary silica particles are about 1.5 nm in size and are aggregated to form secondary particles with definite spherical form. The diameter of these secondary particles is very variable.

20 Tertiary aggregate structure comprises the former particulates and is characterized by the random packing of secondary particles of discrete form and variable size, lacking the chain-like structure of TYPE I. The presence of secondary inter-particulate bridging silica is less evident than for TYPE I, (fig. 4 & 5 of New Zealand Patent 232170/228472 and EO 0396242).

25 TYPE II precipitated silica is morphologically consistent with pyrogenic silicas made under anhydrous conditions e.g. arc or plasma silicas.

TYPE III Precipitated silica possessing primary, secondary and tertiary aggregate structure.

30 Primary particle size is about 1.5 nm. Secondary particulate silica composed of the primary particles is both variable in size and shape.

Secondary particulate silica of TYPE I and TYPE II is present.

- 5 -

Tertiary aggregate structure combines characteristics of both TYPE I and TYPE II silicas. Tertiary aggregate structure is best characterized as diverse, lacking uniformity of secondary particle size and shape but having secondary particulate bridging silica present.

- 5 The TYPE III precipitated silica may contain secondary particulate silica and bridging material with equivalent circular or cross-sectional diameters significantly larger than TYPE I precipitated silica, (fig. 6 & 7 of New Zealand Patent 232170/228472 and EP 0396242).

10 All of these novel types of tertiary aggregate amorphous silicas are recoverable from geothermal water by the practice of this invention by controlling the conditions of polymerization of the silicic values contained therein, the conditions of the growth of the primary and secondary particles of polymerized silica, and the conditions of precipitation of the polymerized silicas. The controls which are required will be detailed hereinafter.

- 15 Primary particles which are small rod like entities of about 1.5 nm in size, bond together to form secondary particles which are essentially spherical. In Type I silica these secondary particles are bound together by substantial amounts of bridging silica to form chain like entities with a tertiary aggregate structure. In Type II silica the essentially spherical secondary particles generally grow to a
20 larger size and are not substantially bridged. Type II secondary particles are structurally consistent with commercial pyrogenic silicas made by steam hydrolysis of SiCl_4 . Type III silica has a combination of Type I and Type II characteristics.

- A colloidal silica sol initially contains particles of the primary type. However, aggregation of these primary particles, to form secondary particles
25 which are approximately spherical, occurs throughout the entire period of aging and/or when electrostatic dispersive forces are reduced through introduction of a suitable precipitation or coagulation agent which may be amorphous silica of Type I, II or III. In the dispersed state, the secondary particles also constitute a colloidal silica sol, although this may not remain stable with time; i.e. precipitated
30 silica may settle.

 The sol so formed for Types I and III silicas consists of secondary particles together with primary particles in various stages of aggregation (see Figures 1-3

- 6 -

and 6-7 New Zealand Patent No. 232170/228472). Aggregation of, and in-fill between, secondary spheroidal particles and accretion of the same is consistent with the low solubility of this region with respect to amorphous silica, due to the negative radius of curvature occurring when any two spheroidal particles approach one another. However, for Type II silica, the development of secondary particles is essentially complete (see Figures 4 and 5 New Zealand Patent No. 232170/228472). These stages of aggregation are consistent with the presence of secondary particulate silica of variable shape and form in the final, substantially tertiary aggregate structure produced from the destabilization and precipitation of the silica in these sols. If a Type I, II or III amorphous silica is used as the precipitation agent, newly formed primary particles are recovered onto the surface of this precipitation agent thereby yielding a Type I, II or III silica product respectively with a larger secondary particle size.

Geothermal waters vary from location to location. However, such waters can be generically characterized as having a neutral to slightly alkaline pH. In addition to the dissolved siliceous values, mainly silicic acid, these waters often have significant concentrations of other ions, such as, for example: sodium, potassium, lithium, magnesium, rubidium, cesium, boron, chloride, and arsenic. These waters also often contain dissolved gaseous species, such as, for example: H_2S , CO_2 , and NH_3 . Table 1 of New Zealand Patent No. 232170/228472 shows typical chemical analyses of representative geothermal waters from several wells in the Kawerau geothermal field.

It has been conventional to use these high temperature geothermal waters as an energy source. That is, the heat in the water is converted to other power embodiments, such as steam and/or electricity. Of course, as the heat in the geothermal water is converted to a more useful form, the temperature and pressure of the water becomes reduced, and most salts contained therein become less soluble. The dissolved salts often precipitate in an uncontrolled manner fouling the tanks and equipment with which they are in contact. The siliceous values in the cooled geothermal water can precipitate out as silicates, sometimes iron silicate, which is not a particularly valuable material. Often, the most problematic mineral which forms upon cooling is a small amount of the available

- 7 -

siliceous values which deposits as a hard, dense vitreous amorphous silica scale with no defined structure.

Further, since the spent waters, after recovering their energy values are often reinjected into the formation, these cooled, lower pressure waters have a
5 higher effective content of dissolved and suspended materials. When this water is reinjected, it is sometimes detrimental to the field in that some of the less soluble salts tend to precipitate or deposit out as scale, such as amorphous silica, calcite and barium sulfate. Such mineral deposits contribute to the clogging of reinjection pipes, wells and the underground formations about the reinjection
10 area.

Arsenic is generally present in geothermal waters. This is an inconvenient and often detrimental component of the geothermal water because it can be toxic to certain environments. The uncontrolled precipitation of the dissolved ions in the geothermal water is also accompanied by the coprecipitation of arsenic values
15 along with the various salts. Even where efforts are made to control the precipitation conditions and to thereby make a desirable silica product, unless special precautions are taken, the arsenic tends to coprecipitate along with, and be adsorbed on the surface of, the silica. This arsenic contamination of the precipitated silica can be a substantial problem, depending on the use to which
20 the silica is to be put. Thus, at least for some end uses, procedures must be adopted to reduce or eliminate the arsenic contamination of the silica product. For example, when the silica product of this invention is to be used in paper coating or impregnation applications, the arsenic content of the precipitated silica should be maintained at a level such that, in the final paper product, the arsenic
25 concentration is below about 2 mg.kg⁻¹ of paper (see New Zealand Patent No. 232170/228472).

DISCLOSURE OF THE INVENTION

It is an object of this invention to provide means for treating geothermal,
30 or other comparable, water in a manner such that amorphous silica is precipitated therefrom in a controlled manner.

It is another object of this invention to recover special forms of amorphous

- 8 -

silica from geothermal water as part of an energy recovery operation.

It is still another object of this invention to substantially prevent, or at least retard the formation of uncontrolled precipitates of silicas, or other salts, onto process equipment, simultaneous to the above objectives.

5 It is still another object of this invention to provide novel forms of particulate amorphous silicas. These silicas can possess a unique combination of enhanced oil absorption and enhanced optical or light scattering properties compared with those of commercial silicas and silicates, and can therefore be used in applications where oil absorption, opacity and reactivity are important.

10 It is a further object of this invention to identify uses of the novel solid particulate silicas made and recovered from dissolved siliceous species in geothermal water.

Other and additional objects of this invention will become apparent from a consideration of this entire specification, including the drawings hereof and the
15 claims appended hereto.

The invention also recognises the use of silica of Type-I, Type-II or Type-III as a heterogeneous precipitation agent or substrate to recover dissolved siliceous values from hot separated geothermal water thereby limiting if not preventing the deposition of silica onto the surfaces of geothermal heat
20 exchangers and process equipment.

The ability to control secondary particle size of Type-I, Type-II or Type-III silica accordingly, as detailed hereinafter by the examples and TEM photographs for Type-I silica (Figures 10-14) by appropriate exposure of precipitated silica to an amount of incoming freshly separated geothermal water is also another aspect
25 of the present invention.

The option of preparing a precipitated silica of Type-I, Type-II or Type-III structure accordingly, by the process described in New Zealand Patent No. 232170/228472 and adding said precipitated silica to the hot geothermal water prior to, at, or immediately after the steam/water separators or energy recovery
30 devices, to recover dissolved siliceous values in the hot geothermal water onto the said precipitated silica in order to protect separators and geothermal process equipment from silica deposition is also an aspect of the present invention.

- 9 -

An alternative and/or option is using a portion of the Type-I, Type-II or Type-III silica harvested from the silica recovery operation downstream of the separators and/or energy recovery devices, for use as the precipitation agent or reactive substrate prior to, at, or immediately after the steam/water separators and/or energy recovery devices. Another aspect is the option of using as the precipitation agent or reactive substrate, a stabilised sol or a slurry of silica particles of Type-I, Type-II or Type-III structure, a gel or a fine powder of silica of Type-I, Type-II or Type-III structure and also the use of other non-silica but receptive materials, either as a slurry, gel or powder.

Another aspect is the ability to recover additional energy from a hot geothermal fluid stream. In most geothermal developments energy recovery is limited by consideration of silica deposition where reinjection of separated water is required. Additional energy can be recovered with the inclusion of silica precipitation according to this invention. This is possible by the provision of a hot separated geothermal fluid with a much decreased potential to deposit silica therefrom onto the surfaces of geothermal heat exchangers and process equipment (eg. reinjection pipes, wells and formation rock) thereby enabling more energy to be recovered from such water than would be the case if the silica was not removed. Such energy may be recovered as electricity by extended flash and/or binary cycle heat exchange, dual or multi pressure condensing turbines or as heat energy by direct heat exchange.

Another aspect is the ability to recover additional minerals from a hot geothermal water stream. This is possible by a provision of a hot separated geothermal fluid/water with a much decreased potential to deposit silica therefrom onto the surfaces of geothermal heat exchangers and chemical process equipment, thereby providing the opportunity to recover additional minerals from the water. This would generally not be possible if the silica, which has the potential to deposit from the cooled water stream was not removed as such silica deposits interfere with and prevent the operation of any additional mineral recovery equipment/process.

A most important aspect of the invention is the provision of a separated geothermal water effluent stream which has a much reduced tendency to deposit

- 10 -

silica therefrom in downstream piping and reinjection wells. The processed geothermal water (34 in attached Figure 5) in which the level of polymeric silica has been substantially reduced by removal as a silica product of Type-I, Type-II or Type-III in the silica plant 30 leaves the remaining dissolved siliceous values essentially as monomeric silica. Such monomeric silica has a much reduced tendency to polymerize further and deposit in downstream piping and in re-injection wells.

An aspect of this invention is in a process where a fluid is derived from an underground source, said fluid being extracted or extractable from the underground source as a hot high pressure geothermal source fluid having dissolved siliceous values therein and said geothermal source fluid is processed by the following steps A1 and A2:

A1 - first flashing the hot, high pressure geothermal source fluid to a lower pressure and temperature to produce steam and to form a second fluid which is at a lower pressure and temperature, or causing a multiplicity of flashes and/or heat exchange to produce second fluid(s) which is or are at a lower pressure and temperature, and which has or have a higher effective concentration of siliceous values dissolved therein, said steam being vented, used in a heat exchanger and/or used in a turbine or turbines; and

A2 - recovering particles of tertiary aggregate amorphous silica from said second fluid(s) by a process which comprises:

- i) whether by parameters of step A1 and/or otherwise, ensuring the relative amounts of said siliceous values and any precipitation agent contained in said second fluid(s) are insufficient to cause substantial quantities of said siliceous materials to come out of solution in said second fluid(s);
- ii) adjusting to and/or maintaining the pH of said second fluid(s) up to about 9.5 during at least the following sequential steps (iii), (iv) and (v);
- iii) forming a silica sol by causing (whether by step A1 and/or otherwise) or having allowed said second fluid(s) to become supersaturated with respect to amorphous silica and initiating polymerisation of said siliceous values therein into polymeric material comprising primary

- 11 -

particles of polymeric amorphous silica without causing substantial quantities of said siliceous values, including polymers thereof, to independently precipitate;

- 5 iv) ageing said silica sol, by holding such for a time and under conditions sufficient to cause and/or to continue polymerisation of said siliceous materials in said sol into said polymeric material and into larger particles thereof, without causing substantial quantities of said polymeric material and/or said particles to independently precipitate;
- 10 v) adding to said silica sol a sufficient quantity of at least one precipitation agent to provide a sufficient proportion thereof, in relation to said polymeric and particulate material, to convert said polymeric material and said particles into silica particles having a tertiary aggregate structure of Type-I, Type-II or Type-III, of an amount sufficient to cause rapid precipitation thereof from said silica sol, thereby precipitating at least some
- 15 of said tertiary aggregate amorphous silica particles to form a slurry of said particles; and
- vi) separating said slurry into at least a first portion (which may still include water) comprising said particles and a second portion comprising a more dilute aqueous medium,
- 20 **a process** ensuring a reduction of the amount of siliceous material which precipitates or deposits out of said geothermal source fluid and/or any fraction thereof on to internal surfaces of apparatus (including piping or channels) used to carry out the process of steps A1 and A2 or at least step A2, which comprises:
- 25 **(I)** introducing into the second fluid(s) in an amount that until step A2(v) is reached does not lead to any substantial independent precipitation, quantities of silica particles having the tertiary aggregate structure of said Type-I, Type-II or Type-III to be subsequently precipitated out by step A2(v) in a quantity and of a size of particle whereby dissolved siliceous materials in said second geothermal fluid(s) accrete to said added particles but do not substantially precipitate out on
- 30 to the internal surfaces of said apparatus (including any piping or channels), thereby at least reducing the amount of siliceous values adhering to said apparatus (including any piping or channels) as well as enlarging said added particles of

- 12 -

tertiary aggregate amorphous silica of the particular form (Type-I, Type-II or Type-III) added and subsequently with step A2(vi), after the addition of at least one said precipitation agent (which may comprise or include still additional quantities of silica particles of the desired tertiary aggregate structure) recovering
5 said grown added particles of tertiary aggregate amorphous silica of the particular Type-I, Type-II or Type-III;

(II) introducing into the second fluid(s) in an amount that until step A2(v) is reached does not lead to any substantial independent precipitation, quantities of receptive substrate particles in a quantity and of a size of particle whereby
10 dissolved siliceous materials in said second geothermal fluid(s) accrete to said added particles but do not substantially precipitate out onto the internal surfaces of said apparatus (including any piping or channels) thereby at least reducing the amount of siliceous values adhering to said apparatus (including any piping or channels) as well as enlarging said added particles by the addition of amorphous
15 silica thereto and subsequently with step A2(vi) after the addition of at least one precipitation agent (which may comprise or include quantities of silica particles of the desired tertiary aggregate structure Type-I, Type-II or Type-III) recovering said grown particles; or

(III) introducing into the second fluid(s) in an amount that until step A2(v) is reached does not lead to any substantial independent precipitation quantities of silica particles having the tertiary aggregate structure of said Type-I, Type-II or Type-III to be subsequently precipitated out by step A2(v) sequentially added or recycled from step A2(vi) in a quantity and of a size of particle where dissolved siliceous materials in said second geothermal fluid(s) accrete to said added
25 particles but do not substantially precipitate out onto the internal surfaces of said apparatus (including any piping or channels) thereby at least reducing the amount of siliceous values adhering to said apparatus (including any piping or channels) as well as enlarging said added particles and subsequently with step A2(vi) after the addition of at least one precipitation agent (which may comprise or include still
30 additional quantities of silica particles of the desired tertiary aggregate structure, sequentially added or recycled or otherwise) recovering said grown added particles of tertiary aggregate amorphous silica of the particular Type-I, Type-II or Type-

- 13 -

III.

Preferably, part of said first portion of step A2(vi), whether as a slurry, gel or powder, is sequentially added or recycled in a controlled amount.

Preferably, said sequential addition or recycle at least in part is between a first flashing and a second flashing and/or heat exchange of step A1.

Preferably, said sequential addition or recycle at least in part is to the first flashing of step A1.

Preferably, said amorphous silica is of Type-I.

Preferably, the amorphous silica is of Type-II.

Preferably, the amorphous silica is of Type-III.

Preferably the amorphous silica is of Type I, Type II or Type III tertiary aggregate structure with an average secondary particle dimensions up to about 30 nm. and an oil absorption of greater than about $190 \text{ g.}100\text{g}^{-1}$ as measured by the spatula rubout method using linseed oil, and a light scattering coefficient greater than about $280 \text{ m}^2.\text{kg}^{-1}$, and a reflectance of greater than about 95% at a wavelength of 557 nm.(using illuminant D65 and 10° viewing angle),and a BET surface are of greater than about $4\text{m}^2.\text{g}^{-1}$.

Preferably, said siliceous values in said source fluid comprises silicic acid.

Preferably, said source fluid comprises silicic acid in a concentration of about 400 to 1,400 mg/kg.

Preferably said source fluid comprises said source fluid in combination with a synthetic source of silicate ion and/or silicic acid in a concentration which exceeds about 400 mg.kg^{-1} .

Preferably, said apparatus is part of an electricity generating system and said steam drives at least one turbine.

Preferably, step A1 includes a first flashing and either a second flashing or heat exchange and Type-I, Type-II or Type-III silica added by the improvement is at least added between said primary flashing and said secondary flashing or heat exchange.

Preferably, the second fluid to be reacted with said precipitation agent or substrate resulting from said secondary flashing or heat exchange is at a temperature of from 30°C to 100°C and has had a preformed silica addition

- 14 -

thereto in a ratio from 0.1 - 10 g of preformed silica per kg of said geothermal fluid.

Preferably, said ratio is from 0.5 - 5g.

Preferably, said second fluid is reacted (preferably in a precipitation
5 reactor) to provide an oxygen free residence time of up to about 30 minutes.

Preferably, after said residence time preferably in said precipitator the fluid is conditioned preferably in a conditioner after flocculent addition which is the precipitation agent added with step A2(v).

Preferably, the residence time in the conditioner after flocculent addition is
10 up to about 5 - 10 minutes.

Preferably, the fluid and/or precipitate from said conditioner is clarified preferably in a clarifier and the main silica carrying fraction thereof is separated from a lesser silica-containing liquid fraction.

Preferably, the lesser silica containing fraction is subjected (optionally after
15 further removal of particulate silica by filtering, settling or otherwise) to re-injection or alternative disposal.

Preferably, the silica product extracted from the main silica-containing fraction or included therein has a BET surface area of at least $4 \text{ m}^2.\text{g}^{-1}$.

Preferably, at least part of the main silica-containing liquid fraction is
20 recirculated into the precipitator.

Preferably, Type-I, Type-II or Type-III silica is introduced between said primary flashing and said secondary flashing or heat exchange and is from an untreated source fluid, ie. is of a type created by a process as claimed in a claim of New Zealand Patent Specification No. 232170/228472 which has not involved
25 any reaction with any externally introduced silica particles.

A further aspect of this invention is a process of producing particles of amorphous silica having a tertiary aggregate structure selected from at least one member of the group consisting of Type-I, Type-II or Type-III, which comprises:

providing a source fluid containing siliceous materials and an amount of a
30 precipitation agent for said siliceous materials which is insufficient to cause substantial quantities of said siliceous materials to come out of solution in said source fluid;

- 15 -

maintaining the pH of said fluid at up to about 9.5 during the following steps;

forming a silica sol, by causing said source fluid to become supersaturated with respect to amorphous silica and initiating polymerization of said siliceous materials therein into polymeric material comprising primary particles of
5 polymeric amorphous silica, without causing substantial quantities of said siliceous materials to be independently precipitated;

aging said silica sol, by holding such for a time sufficient to continue the polymerization of said siliceous materials in said sol into said polymeric material,
10 without causing substantial quantities of said polymeric material to be independently precipitated;

adding to said silica sol a sufficient quantity of at least one of said precipitation agents to provide a sufficient proportion thereof, in relation to said polymeric material, to convert said polymeric material into silica particles having a
15 tertiary aggregate structure of said Type-I, Type-II or Type-III, of an amount sufficient to cause rapid precipitation thereof from said silica sol;

thereby precipitating at least some of said tertiary aggregate amorphous silica particles to form a slurry of said particles;

harvesting at least a portion of said particles; and

20 sequentially adding or recycling at least a portion of said particles into admixture with said geothermal source fluid prior to said precipitation stage in an amount such that dissolved siliceous materials in said geothermal fluid are converted into primary particles and precipitate on to said sequentially added or recycled particles and cause them to grow to a larger effective secondary particle
25 size.

Preferably, said process includes sequentially adding or recycling said particles as a slurry.

Preferably, said process includes sequentially adding or recycling said particles into admixture with said source fluid prior to supersaturation thereof
30 with respect to amorphous silica.

Preferably, said source fluid is a geothermal source fluid.

Preferably, said process includes recycling said particles into admixture with

- 16 -

said source fluid prior to aging thereof.

Preferably, said process includes recycling said particles into admixture with said source fluid after aging thereof.

- Preferably the admixture of geothermal source fluid and tertiary aggregate
- 5 Type I, II, or III silica which is to be harvested, is further treated with said precipitation agents to effect complete precipitation and yield effluent of low suspended solids.

- Preferably the admixture of geothermal source fluid and tertiary aggregate
- 10 Type I, II, or III silica which is to be harvested, is treated with equivalent solution concentrations of up to 5mg.kg^{-1} polyethylene oxide and up to 5mg.kg^{-1} of a high charge density polyamine, in order to effect complete precipitation and yield effluent of low suspended solids.

- A further aspect of the invention is, in a process of recovering energy from a hot, high pressure geothermal source fluid, containing dissolved siliceous values
- 15 therein, derived from an underground source, which process comprises;

- first flashing source fluid to a substantially lower pressure and temperature to produce high pressure steam and to form a second fluid which is at a lower temperature and pressure and therefore has a higher effective concentration of siliceous values dissolved therein;

- 20 converting said high pressure steam to electricity;
- and

recovering particles of tertiary aggregate amorphous silica from said second fluid by a process which comprises:

- causing the relative amounts of said siliceous values and any precipitation
- 25 agent contained in said second fluid to be insufficient to cause substantial quantities of said siliceous materials to come out of solution in said second fluid;

maintaining the pH of said second fluid at up to about 9.5 during the following steps;

- forming a silica sol, by causing said second fluid to become supersaturated
- 30 with respect to amorphous silica and initiating polymerization of said siliceous values therein into polymeric material comprising primary particles of polymeric amorphous silica, without causing substantial quantities of said siliceous values,

- 17 -

including polymers thereof, to independently precipitate;

ageing said silica sol, by holding such for a time sufficient to continue the polymerization of said siliceous values in said sol into said polymeric material and into larger particles thereof, without causing substantial quantities of said

5 polymeric material or said particles to independently precipitate;

adding to said silica sol a sufficient quantity of at least one precipitation agent to provide a sufficient proportion thereof, in relation to said polymeric and particulate material, to convert said polymeric material and said particles into silica particles having a tertiary aggregate structure of said Type-I, Type-II or

10 Type-III, of a size sufficient to cause rapid precipitation thereof from said silica sol;

thereby precipitating at least some of said tertiary aggregate amorphous silica particles to form a slurry of said particles; and

separating said slurry into at least a first portion comprising said particles
15 and a second portion comprising a more dilute aqueous medium;

the process to at least substantially reducing the amount of siliceous material which precipitates out of said geothermal source fluid on to internal surfaces of apparatus and piping used to carry out this process, which comprises:

recycling a portion of said separated particles into admixture with said
20 geothermal source fluid, in a proportion, taking into account the amount of siliceous values in said source fluid, sufficient to provide at least a critical coagulant concentration, prior to said flashing in an amount such that dissolved siliceous materials in said geothermal fluid accrete to said particles but do not substantially precipitate out onto the internal surfaces of said apparatus and
25 piping, thereby at least reducing the amount of siliceous values precipitated on and adhering to said apparatus, as well as enlarging said sequentially added or recycled particles of tertiary aggregate amorphous silica; and

recovering at least a portion of said enlarged particles of tertiary aggregate amorphous silica.

30 Preferably, said process includes subjecting said geothermal source fluid to a first, high pressure flashing to produce high pressure steam and a first aqueous liquid underflow at lower elevated pressure and temperature than said source

- 18 -

fluid which contains said siliceous values; subjecting said underflow to a second, lower pressure flashing to produce lower pressure steam and a second aqueous liquid underflow; converting said steam to electricity; recovering siliceous values from said second underflow; and recycling a portion of said particulate product, in
5 slurry form, into admixture with said first underflow.

Preferably, said process includes subjecting said geothermal source fluid to a first, high pressure flashing to produce high pressure steam and a first aqueous liquid underflow at lower elevated pressure and temperature than said source fluid which contains said siliceous values; subjecting said underflow to a second,
10 lower pressure flashing to produce lower pressure steam and a second aqueous liquid underflow; converting said steam to electricity; recovering siliceous values from said second underflow; and recycling a portion of said particulate product, in slurry form, to said high pressure flashing.

Preferably, said steam from said first flashing drives a high pressure,
15 electricity generating turbine which produces a spent stream, comprising lower pressure and temperature steam; and driving a second, lower pressure, electricity generating turbine with both said spent stream and said steam from said second flashing.

Preferably, said improved process includes reinjecting said more dilute
20 aqueous medium into the underground source of said geothermal source fluid.

Preferably, said source fluid contains minerals in addition to siliceous values, and including the further step of, after recovering said particulate silica and forming said more dilute aqueous medium, recovering at least a portion of said additional minerals from said more dilute aqueous medium.

25 Preferably, said geothermal source fluid contains arsenic values, and wherein said improved process produces a particulate amorphous silica product which contains less arsenic than would particulate silica recovered from said source fluid without said sequential addition or recycle.

Preferably, said geothermal source fluid contains arsenic values, and
30 wherein said process produces a particulate amorphous silica product which contains less arsenic than would particulate silica recovered from said source fluid without growth via this process.

- 19 -

The invention is also the product(s) of any one of the preceding processes.

The invention also comprises paper containing the product in admixture with the fibres thereof or paper having the product disposed on the surface thereof.

5 Another aspect of this invention is a process for the formation and recovery of special amorphous silicas from geothermal waters, or the like. According to this aspect of this invention, amorphous silica having a tertiary aggregate structure, selected from at least one member of the group consisting of Type-I, Type-II and Type-III, as will be hereinafter defined, is suitably made by a
10 process including:

 providing a source fluid containing siliceous materials and an amount of a coagulation or precipitation agent for siliceous materials, selected from the group consisting of at least one cation, at least one cationic polymer, at least one cationic flocculent, at least one non-ionic flocculent, and previously produced
15 amorphous silica of the type sought to be produced, which is insufficient to cause substantial quantities of said siliceous materials to come out of solution in said source fluid;

 adjusting the pH of the fluid to up to, but not substantially more than, about 9.5, and maintaining such in this pH range during the following steps;
20 causing said source fluid to become supersaturated with respect to amorphous silica and initiating polymerization of said siliceous materials therein into polymeric material comprising primary particles of polymeric amorphous silica, without causing substantial quantities of said siliceous materials to be precipitated, to thereby form a silica sol, particularly a substantially stable silica
25 sol;

 ageing said silica sol, by holding such for a time sufficient to continue the polymerization of said siliceous materials in said sol into said polymeric material, including polymeric silicas of larger size than the primary particles made in the supersaturation step set forth above, without causing substantial quantities of said
30 polymeric material to be precipitated at that time; and

 then adding to said silica sol a sufficient quantity of at least one of said precipitation and/or coagulation agents to provide a sufficient concentration

- 20 -

thereof, in relation to said polymeric material, to convert said polymeric material into silica particles having a tertiary aggregate structure of said Type-I, Type-II or Type-III and to cause rapid precipitation thereof from said silica sol.

In a further aspect the invention consists in a silica product having tertiary
5 aggregate structure with an average secondary particle dimensions
up to about 30 nm. and an oil absorption of greater than about 190 g.100g^{-1} as
measured by the spatula rubout method using linseed oil, and a light scattering
coefficient greater than about $280 \text{ m}^2.\text{kg}^{-1}$, and a reflectance of greater than about
95% at a wavelength of 557 nm.(using iluminant D65 and 10° viewing angle), and
10 a BET surface area of greater than about $4 \text{ m}^2.\text{g}^{-1}$.

In another aspect the invention is a silica product obtained from
geothermal water having a tertiary aggregate structure with an average secondary
particle dimensions up to about 30 nm. and an oil absorption of greater than
about 190 g.100g^{-1} as measured by the spatula rubout method using linseed oil,
15 and a light scattering coefficient greater than about $280 \text{ m}^2.\text{kg}^{-1}$, and a reflectance
of greater than about 95% at a wavelength of 557 nm.(using iluminant D65 and
 10° viewing angle), and a BET surface area of greater than about $4 \text{ m}^2.\text{g}^{-1}$.

In still a further aspect the invention is a silica product having a Type I, II
or III tertiary aggregate structure with an average secondary particle dimensions
20 up to about 30 nm. and an oil absorption of greater than about 190 g.100g^{-1} as
measured by the spatula rubout method using linseed oil, and a light scattering
coefficient greater than about $280 \text{ m}^2.\text{kg}^{-1}$, and a reflectance of greater than about
95% at a wavelength of 557 nm.(using iluminant D65 and 10° viewing angle), and
a BET surface area of greater than about $4 \text{ m}^2.\text{g}^{-1}$.

25 In another aspect the inventions is a silica product obtained from
geothermal water having a Type I, Type II or Type III tertiary aggregate structure
with an average secondary particle dimensions up to about 30 nm. and an oil
absorption of greater than about 190 g.100g^{-1} as measured by the spatula rubout
method using linseed oil, and a light scattering coefficient greater than about 280
30 $\text{m}^2.\text{kg}^{-1}$, and a reflectance of greater than about 95% at a wavelength of 557
nm.(using iluminant D65 and 10° viewing angle), and a BET surface area of
greater than about $4 \text{ m}^2.\text{g}^{-1}$.

- 21 -

In another aspect the invention is the use of a silica product in paper whereby paper filled with the silica product has an increased opacity by at least 1 point, an increase in brightness of at least 1 point and a reduction in the printed opacity of at least 15% for each one % weight/weight addition of Type I silica,
5 compared with paper prepared from the same pulp furnish and made under the same conditions but without the addition of Type I silica.

In yet another aspect the invention is a silica product which when added in an amount up to about 30 kg/tonne to newsprint of basis weight of about 35 gsm or greater results in an increased opacity by at least 1 point, an increase in
10 brightness of at least 1 point and a reduction in the printed opacity of at least 15% for each one % weight/weight addition of silica, compared with paper prepared from the same pulp furnish and made under the same conditions but without the addition of silica.

Another aspect of the inventions is a composite particle which has a core
15 of another material, such as clay, calcium carbonate etc, around which or onto which a coating of silica is deposited by the process of recovering silica from geothermal water as claimed in anyone of claims 1 to 38.

Another aspect is paper coated with a coating formulation and/or
20 impregnated with a formulation which has as one of its components Type I,II or III silica made by a process of the invention.

Another aspect is cement or cementitious products, including concrete to which Type I, Type II or Type III silica made by a process of the invention has been added as one of the components of the mix.

25 Another aspect is paint with a formulation which has as one of its components Type I,II or III silica made by a process the invention.

Another aspect is rubber having as a one of its components Type I,II or III silica made by a process of the invention.

Another aspect is a filler composition having as its principal active
30 component Type I,II or III silica made by a process of the invention.

Yet another aspect is a substantially inert extender composition having as its principal active component Type I,II or III silica made by a process of the

- 22 -

invention.

Yet a further aspect is a thixotropic agent having as its principal active component Type I,II or III silica made by a process of the invention.

Another aspect is an opacifier composition having as its principal active component Type I,II or III silica made by a process of the invention.

Another aspect is an absorbent comprising Type I,II or III silica made by a process of the invention.

Another aspect is an adhesive composition having as its principal active component Type I,II or III silica made by a process of the invention.

In a further aspect the invention is a method of applying an agricultural chemical to land which comprises absorbing said agricultural chemical onto the surface of particles of Type I,II or III silica made by a process of the invention.

Another aspect is an anticaking agent having as its principal active component Type I,II or III silica made by a process of the invention.

Another aspect is a battery separator having as its principal active component Type I,II or III silica made by a process of the invention, and/or toothpaste having as one of its active components Type I,II or III silica made by a process of the invention, and/or

a ceramic composition or formulation having as one of its components Type I,II or III silica made by a process of the invention.

Another aspect is a mineral recovery process which utilises as its feed stock geothermal water from which the dissolved silica has been recovered substantially or in part, by a process of the invention.

Preferably the dissolved silica in geothermal water is removed substantially or in part thereby forming a more dilute aqueous solution and thereafter providing said more dilute aqueous solution to a further process for the removal in part or otherwise of other dissolved minerals or components in said solution.

In a further aspect the invention is the use of a silica product in paper whereby paper filled with the silica product has an increased opacity by at least 1 point, an increase in brightness of at least 1 point and a reduction in the printed opacity of at least 15% for each one % weight/weight addition of silica, compared with paper prepared from the same pulp furnish and made under the same

- 23 -

conditions but without the addition of silica.

In all cases the term "**recycle**" is taken to mean returning some or all of the precipitated silica either as a slurry, concentrated or otherwise, or solid particles to the commencement of the silica recovery operation where said precipitated silica slurry or particles are exposed to fresh geothermal water, and also where said precipitated silica slurry or particles are exposed to fresh (aged) geothermal water in one or more (cascaded or sequential) silica recovery operations, or a continuous flow or similar type reactor system.

In accord with and fulfilling the objects of this invention, another aspect of this invention comprises the amorphous silicas produced by this process. Silicas which are substantially the same as those produced by this process, but produced by different processes, or by variants in the instant described process, are also considered to be included within this aspect of this invention. These Type I, II or III amorphous silicas have a distinct microstructure which is discernable from electron photomicrographs thereof.

The precipitated amorphous silicas of this invention are classified according to the Type I, II or III structure they possess. These structures have been described fully in New Zealand Patent No. 232170/228472

The principal differences in structure of precipitated silicas which have been made according to the present invention, compared to those made according to New Zealand Patent No. 232170/228472, involve the nature of the secondary particles, or particulate system, and the resultant tertiary aggregate structure. Transmission electron microscopy has not resolved a primary particle size difference for the Type I, II or III precipitated silicas. Secondary silica particle morphology, and therefore, tertiary aggregate particle structure, as developed from aqueous solution experiments, can be influenced by the stage of polymerization of the silica values at which a coagulating/ precipitating agent is introduced into the process stream.

This invention may also be said broadly to consist in the parts, elements and features referred to or indicated in the specification of the application, individually or collectively, and any or all combinations of any two or more of said parts, elements or features, and where specific integers are mentioned herein

- 24 -

which have known equivalents in the art to which this invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

5 BRIEF DESCRIPTION OF THE DRAWINGS

The invention consists in the foregoing and also envisages constructions of which the following gives examples.

Preferred forms of the present invention will now be described with reference to the accompanying drawings in which:

10 Figures 1 through 8 are several schematic block flow diagrams of different process embodiments of this invention;

Figure 9 is a graphical representation of the rate at which monomeric silica values can be removed from geothermal source fluid in the presence of reactive slurried particles of type I tertiary aggregate amorphous silica;

15 Figure 10 is photomicrograph of Type-I silica starting material;

Figure 11 is a photomicrograph of Type-I silica after five reactions;

Figure 12 is a photomicrograph of Type-I silica after ten reactions;

Figure 13 is a photomicrograph of Type-I silica after fifteen reactions;

Figure 14 is a photomicrograph of Type-I silica after twenty reactions;

20 Figure 15 is a plot of average secondary particle dimension against controlled growth of Type-I silica by recycle or sequential reactions;

Figure 16 is a flow diagram showing a preferred process from a geothermal source fluid that has been subjected to a first flashing through to a silica product, the resulting fluid capable of being re-injected or alternative disposal and also
25 having the capability of providing for the generation of electricity, the schematic diagram being of a continuous process with provision for recycle or sequential reactions; and

Figure 17a and 17b are diagrams presenting spectral reflectance from 400-700 nm. for Type I silica, and for Tokusil (a commercial silica filler) and Alphatex
30 (a commercial calcined clay filler); Figure 17a is for Type I silica with a 14 and a 27 nm. secondary particle size, made according to Process Example 1, Tokusil and Alphatex; Figure 17b is for Type I silica (Geosilica) with a 18 nm. secondary

- 25 -

particle size, made according to Process Example 8, Tokusil and Alphatex.

BEST MODES FOR CARRYING OUT THE INVENTION

In this invention the controlled precipitation of silica yields products with
5 particular properties which make them suitable for a number of specific
commercial applications, such as for example in paper filling, paper coating, paint,
rubber, cement, anticaking agent, thixotropic agents, opacifying agents, extender
agents, component of battery separators, inert fillers and inert carrier applications.

The secondary and tertiary particle size, pore characteristics, surface
10 hydroxyl, that is silanol group density, chemical purity and optical quality of the
silica product can be controlled by the practice of this invention. Such controlling
factors include aging time, stage at which precipitation agent is added, the nature,
type and concentration of the precipitation agent or substrate, the method of
cooling the geothermal water, the cooling rate profile, precipitation temperature,
15 pH of the water, and the equivalent number of reaction steps (recycle or
sequential) used in the process.

It is preferred in the practice of this invention that the source fluid is a
naturally occurring geothermal fluid at an elevated temperature. However, it is
considered to be within the scope of this invention to utilize an aqueous solution
20 of siliceous values which has been synthetically derived, or a naturally occurring
aqueous solution which has been modified to increase or decrease its ion contents
and/or make up. In the case of naturally occurring geothermal fluid it is also
preferred that the source fluid contain about 400 to 1,400 mg of dissolved or
dispersed siliceous values per kg of solution. This concentration of siliceous values
25 can be higher when a modified source fluid is used.

A further object of this invention is fulfilled by the discovery of special uses
to which the silicas of this invention may be put. The silicas of this invention can
be recovered in slurry, cake, or powder form. They can be used in place of silicas
which have been made by conventional processes. However, it has been found
30 that the silicas of this invention have special attributes when used as fillers,
impregnants or coatings for paper. In particular, it has been found that paper
which has been filled with a silica product made according to this invention has

- 26 -

substantially reduced print through (printed opacity), increased opacity (unprinted opacity) and increased brightness compared with paper without silica made by this process, and with paper filled with current commercial silicas and other filler materials. In addition, paper which has been coated with a silica product made according to this invention has substantially better opacity and ink retention in preselected defined areas. The silica product may also be added to paint as an extender for titanium dioxide because of its favourable light scattering properties, and also as a flattening agent and as a rheology modifier.

Other uses to which the silicas of this invention can be put with advantage include, *inter alia*, as an additive in rubbers, a filler for plastic materials, in cements and cementitious compositions such as concrete, in adhesives, as a rheology modifier, and as an anticaking agent. These novel silicas also find excellent application as absorbents, particularly in connection with the distribution of agricultural chemicals and other materials which require a substrate or an additive with specific predeterminable surface absorption characteristics.

According to another aspect of this invention, amorphous silica having a tertiary aggregate structure of Type-I, and having a BET surface area of at least 4 m².g⁻¹, can be made by a method which comprises:

providing an aqueous source fluid containing about 400 to 1,400 mg of dissolved siliceous materials per kilogram of fluid and an amount of a precipitation agent for said siliceous materials, selected from the group consisting of at least one cation, at least one cationic polymer, at least one cationic flocculent, at least one non-ionic flocculent, and previously produced particles of tertiary aggregate Type I silica, which is insufficient to cause substantial quantities of the desired siliceous materials to come out of solution in said source fluid;

adjusting the pH of said fluid to about 5 to 9.5 and maintaining such at these pH levels during the following steps;

forming a stable silica sol, by causing said source fluid to become supersaturated with respect to amorphous silica and initiating

- 27 -

polymerization of said siliceous materials therein into polymeric material comprising primary particles of polymeric amorphous silica, without causing substantial quantities of said siliceous materials to be precipitated;

5 rapidly cooling said silica sol to a lower temperature, which is at least about 30°C;

aging said silica sol, without adding precipitation agent thereto in an amount sufficient to cause substantial precipitation of tertiary aggregate
10 silica particles therefrom, by holding such for a time sufficient to continue the polymerization of said siliceous materials in said sol into polymeric material comprising primary amorphous silica particles which are capable of being converted, by adjusting the concentration of precipitation agent, into tertiary aggregate amorphous silica particles of Type-I structure; and

15 adding to said silica sol a sufficient quantity of at least one of said precipitation agents, in a manner so as not to raise the pH of the system to over about 9.5, to provide a sufficient proportion thereof in relation to said polymeric material to convert said polymeric material into a silica particle
20 having a tertiary aggregate structure of Type-I and to cause rapid precipitation thereof.

Another aspect of this invention involves the formation of amorphous siliceous material having a tertiary aggregate structure of Type-II. This material is made by a method which comprises:

25 providing an aqueous source fluid containing about 400 to 1,400 mg of dissolved siliceous materials per kilogram of fluid and an amount of a precipitation agent for said siliceous materials, selected from the group consisting of at least one cation, at least one cationic polymer, at least one cationic flocculent, at least one non-ionic flocculent, and an amount of
30 previously produced particles of tertiary aggregate Type II silica which is insufficient to cause substantial quantities of said siliceous materials to come out of solution in said source fluid;

- 28 -

forming a stable silica sol, by causing said source fluid to become supersaturated with respect to amorphous silica, and initiating polymerization of said siliceous materials therein into polymeric material comprising primary particles of polymeric amorphous silica, without causing
5 substantial quantities of said siliceous materials to be precipitated;

adding to said sol, prior to there being any substantial decrease in molybdate active silica concentration therein, a sufficient quantity of at least one precipitation agent to cause the conversion of said polymeric
10 amorphous silica into amorphous silica particles of tertiary aggregate structure of Type-II;

adjusting the pH of said fluid at about 5 to 9.5 and maintaining such at this level for the remainder of this process;

15 aging said silica sol at said pH, without adding further precipitation agent thereto in an amount sufficient to cause substantial precipitation of tertiary aggregate silica particles therefrom, by holding such for a time sufficient to continue the polymerization of said siliceous materials in said sol into
20 polymeric material comprising primary amorphous silica particles which are capable of being converted, by adjusting the concentration of precipitation agent, into tertiary aggregate amorphous silica particles of Type-II structure; and

25 then, upon the formation of a quantity of amorphous silica tertiary aggregate particles of structure Type-II sufficient to allow the precipitation thereof, adding to said system a sufficient quantity of at least one of said precipitation agents, in a manner so as not to raise the pH of the system to over about 9.5, to provide a sufficient proportion thereof in relation to said
30 polymeric material to convert said polymeric material into silica particles having a tertiary aggregate structure of Type-II, and to cause the rapid precipitation thereof.

- 29 -

Where the desired product is a Type II amorphous silica tertiary aggregate particle, it has been found to be preferable to employ a source fluid which has been artificially generated. This includes a source fluid which has been naturally produced and which has been modified to either increase or decrease the ion
5 make up and concentration therein.

According to still another aspect of this invention, amorphous silica having a tertiary aggregate structure of Type-III is made by a method which comprises:

providing an aqueous source fluid containing about 400 to 1,400 mg of dissolved siliceous materials per kilogram of fluid and an amount of a
10 precipitation agent for said siliceous materials, selected from the group consisting of at least one cation, at least one cationic polymer, at least one cationic flocculent, at least one non-ionic flocculent, and previously made particles of tertiary aggregate Type III amorphous silica, which is insufficient to cause substantial quantities of said siliceous materials to
15 come out of solution in said source fluid;

forming a stable silica sol, by causing said source fluid to become supersaturated with respect to amorphous silica and initiating
polymerization of said siliceous materials therein into polymeric material
20 comprising primary particles of polymeric amorphous silica, without causing substantial quantities of said siliceous materials to be precipitated;

adding a sufficient quantity of a precipitation agent, or additional precipitating agent as defined above, to said sol, to cause the conversion of
25 said polymeric amorphous silica into amorphous silica particles of tertiary aggregate structure of Type-III and to cause the precipitation thereof from said sol;

adjusting the pH of said fluid to about 5 to 9.5;
30

aging said silica sol at said pH, without adding further precipitation agent thereto, by holding such for a time and under conditions sufficient to cause

- 30 -

additional polymerization of dissolved siliceous materials in said sol into polymeric material comprising primary amorphous silica particles which are capable of being converted, by adjusting the concentration of precipitation agent, into tertiary aggregate amorphous silica particles of Type-III structure; and

then, upon the formation of a quantity of amorphous silica tertiary aggregate particles of Type-III structure sufficient to allow the precipitation thereof, adding to said system further quantities of at least one of said precipitation agents, in a manner so as not to raise the pH of the system to over about 9.5, to provide a sufficient proportion thereof in relation to said polymeric material to convert more of said polymeric material into silica particles having a tertiary aggregate structure of Type-III, and to cause the rapid precipitation thereof.

According to yet another aspect of this invention, amorphous silica having a Type I, Type II or Type III tertiary aggregate structure with an average secondary particle dimension up to about 30 nm. and an oil absorption of greater than about $190 \text{ g.}100\text{g}^{-1}$ as measured by the spatula rubout method using linseed oil, and a light scattering coefficient greater than about $280 \text{ m}^2.\text{kg}^{-1}$, and a reflectance of greater than about 95% at a wavelength of 557 nm.(using illuminant D65 and 10° viewing angle), and a BET surface area of greater than about $4 \text{ m}^2.\text{g}^{-1}$, can be made by a method which comprises:

providing an aqueous source fluid containing about 400 to 1,400 mg of dissolved siliceous materials per kilogram of fluid and an amount of a precipitation agent for said siliceous materials, selected from the group consisting of at least one cation, at least one cationic polymer, at least one cationic flocculent, at least one non-ionic flocculent, and previously produced particles of tertiary aggregate Type I silica, which is insufficient to cause substantial quantities of the desired siliceous materials to come out of solution in said source fluid;

- 31 -

adjusting the pH of said fluid to about 5 to 9.5 and maintaining such at these pH levels during the following steps;

5 forming a stable silica sol, by causing said source fluid to become supersaturated with respect to amorphous silica and initiating polymerization of said siliceous materials therein into polymeric material comprising primary particles of polymeric amorphous silica, without causing substantial quantities of said siliceous materials to be precipitated;

10 rapidly cooling said silica sol to a lower temperature, which is at least about 30°C;

aging said silica sol, without adding precipitation agent thereto in an amount sufficient to cause substantial precipitation of tertiary aggregate silica particles therefrom, by holding such for a time sufficient to continue the polymerization of said siliceous materials in said sol into polymeric material comprising primary amorphous silica particles which are capable of being converted, by adjusting the concentration of precipitation agent, into tertiary aggregate amorphous silica particles of Type-I structure; and

20 adding to said silica sol a sufficient quantity of at least one of said precipitation agents, in a manner so as not to raise the pH of the system to over about 9.5, to provide a sufficient proportion thereof in relation to said polymeric material to convert said polymeric material into a silica particle having a tertiary aggregate structure of Type-I and to cause rapid precipitation thereof.

Preferably the source fluid is a geothermal fluid.

Preferably the concentration of silica in the source fluid is about 400 to 1,400 mg.kg⁻¹ expressed as silica. This preferred concentration promotes spontaneous nucleation. This range of concentrations is often present in geothermal water which is being discharged from a power generation operation in which the power source is the geothermal fluid. Higher silica concentrations do

30

- 32 -

sometimes occur in some geothermal water sources. Processing of these geothermal fluids with such higher silica contents can be carried out in a manner which is substantially similar to that described here. It may be desirable, or even in some cases necessary, to dilute the source fluid or to change its pH in order to
5 be better able to control the onset and rate of polymerization of the dissolved siliceous values to form primary particles. A process stream with lower initial silicic acid concentrations may require lower process temperatures to promote spontaneous nucleation. Preferably the aging of the source fluid is for such time as will cause the initiation of polymerization of the siliceous values within the fluid
10 to form the necessary primary particles which will then be converted to the desired tertiary aggregate particles of this invention.

According to New Zealand Patent No. 232170/228472 where arsenic reduction is required, it has been noted that this can be accomplished by reducing the temperature of the source fluid. Such temperature reduction, however, must
15 not be to an extent sufficient to cause the premature aggregation and precipitation of particulate silica. Within this *caveat* it is acceptable to reduce the temperature of the source fluid, either before, during or after the initial step of aging the source fluid. It is also acceptable to reduce the temperature of the stable silica sol, but not so much as will destabilize the sol. This lowering of the
20 temperature will tend to prevent or retard the coprecipitation of the arsenic with the silica in an amount which is detrimental to the quality of the final product. It has been found that if the source fluid, and/or the silica sol, is left at higher temperature for a long time (refer to Figure 11 New Zealand Patent No.232170/228472) , more arsenic appears to become associated with the silica in
25 the sol and is adsorbed on to the tertiary aggregate silica particles upon its precipitation from the silica sol. Conversely, when the temperature of the source fluid is maintained at a lower temperature for the same time, the amount of arsenic which coprecipitates is substantially reduced.

Where the source fluid includes arsenic values and a temperature reduction
30 step is considered to be desirable in order to limit the amount of arsenic adsorbed onto the precipitating silica, it is preferred to lower this temperature of the source fluid prior to the aging thereof. The adsorption of arsenic onto the surface of

- 33 -

colloidal silica in the sol is believed to be, at least in part, a kinetic temperature dependent relationship. Lowering the temperature of the source fluid as long as possible before the aging step is initiated appears to be effective in reducing arsenic adsorption, and thus, is effective in reducing ultimate arsenic

5 concentrations in the product amorphous silica particles having substantially a tertiary aggregate structure. This is described in detail in New Zealand Patent No. 232170/228472.

As shown in Figure 9, if silica is used as the precipitation agent or substrate, then the dissolved silica is recovered more rapidly from solution than is
10 the case with spontaneous nucleation. In the case where silica is used as the precipitation agent or substrate, dissolved silica is recovered onto the receptive silica surface as primary particles when no additional cationic agents are required. The surface of the precipitated silica therefore comprises relatively pure silica which is significantly ionised at the pH of geothermal water. The silica surface
15 carries significant negative charge and is non receptive to arsenic species, naturally occurring in geothermal water. The arsenic concentrations of silica grown according to this process are lower than that achieved solely due to rapid cooling and the use of cationic precipitation agents. This results in the silica product having a lower arsenic content.

20 In one aspect, the present invention may broadly be said to consist in a method of obtaining precipitated amorphous silica having substantially a tertiary aggregate structure (whether as an aqueous slurry, as a cake, powder, gel or otherwise) and an arsenic concentration lower than that produced by a process which does not utilise silica as a precipitation agent, from a geothermal fluid
25 (natural or induced). Such a said low arsenic-content silica can be made by the said method in which silica is used as the precipitation agent or substrate.

In a further aspect of this invention the temperature of the source fluid is preferably adjusted to, and maintained at or near, about 100°C, and it is rapidly cooled to a lower temperature of at least about 30°C prior to initiating step A2.

30 Organic flocculants can be used to effect complete precipitation of tertiary aggregate silica particles after the reaction of an externally supplied precipitation agent or substrate with fresh geothermal water. It is most appropriate to use a

- 34 -

cationic organic flocculant at higher pH where the silica surface is substantially negatively charged; and a non-ionic organic flocculent when the sol is at or below neutral pH. Under these conditions of lower pH, hydrogen bonding can occur.

In accord with one aspect of this invention, one preferred coagulant
5 composition is a combination of a non-ionic flocculent and a cationic flocculent. In this embodiment, the combination should have relative proportions of about 0 to 5 parts by weight of the non-ionic flocculent, and about 0 to 5 parts by weight of the cationic flocculent per 1,000,000 parts by weight of the source fluid.

One suitable non-ionic material is polyethylene oxide. It has been found to
10 be suitable to use polyethylene oxides of a molecular weight of about 0.2 to 8 million. Examples of these materials are available commercially under the tradename: Union Carbide FRA & Kemira Netbond (FRA & FRB). One suitable cationic flocculent is a high charge density, low molecular weight polyamine. These materials are represented and exemplified by materials which
15 are generally available and sold commercially under the tradename Allied Colloids Magnafloc, such as Magnafloc 368.

It is a further aspect of this invention to use previously prepared particles of tertiary aggregate Type I, II or III amorphous silica as a heterogeneous precipitation agent. The addition of such previously prepared silica particles to a
20 geothermal water source prior to its becoming supersaturated with silica values promotes the formation of new primary particles and causes them to precipitate onto the previously prepared particles of tertiary aggregate silica. The precipitation of the newly formed primary particles takes place during and after the geothermal water becomes supersaturated with respect to amorphous silica. It
25 is completed when the water portion of the geothermal source fluid is separated from the amorphous silica particles which have been grown. The desired siliceous values are thus precipitated from the stable silica sol in a controlled manner.

Particularly, it has been found to be expedient to use, as the heterogeneous precipitation agent, a slurry of particles of previously prepared tertiary aggregate
30 silica of the same type as is sought to be made. That is, if the heterogeneous particles are Type I tertiary aggregate amorphous silica particles, the product which results from practising this aspect of this invention also has this same

- 35 -

microstructure. This in itself is somewhat surprising given that the amorphous precipitation agent has no particular regularity of structure to template from as is the case for crystalline materials.

It is now known from Transmission Electron Microscope studies results of which are shown in Figures 10 - 13 that the new silica growth on the old particles is the addition of further primary particles of amorphous silica to the secondary particles of silica. The formation and accretion of primary particles of pure amorphous silica from a system containing a heterogeneous precipitation agent was an unexpected and remarkable result of the experiments conducted. Prior to this discovery it was known that spontaneous nucleation resulted in the formation of critical size nuclei which further grew to the limiting dimensions of the primary particle as defined here of up to about 1.5 nm. The introduction of a heteronucleation agent results in a system whereby two competing forces exist to remove the available silica; that of homogeneous or spontaneous nucleation and that of heterogeneous nucleation. Prior to these experiments it was not known what form the silica would take when removed on to the heteronucleus or preexisting silica surface. Prior knowledge in this area (Weres et. al., 1980) taught that the kinetics of monomeric silica removal could be explained by molecular deposition of the silica. Molecular deposition of silica would result in an essentially non-porous, dense, vitreous coating of silica on to the pre-existing surfaces. The coating would not contain a primary particulate system. Rather, Transmission Electron Microscopy has revealed that the present invention maintains a primary particulate system and that all silica removed has this primary particle form.

The rate of monomeric silica removal from the geothermal source fluid is substantially greater when a higher amount of receptive solid surfaces are present as compared to the rate at which spontaneous nucleation occurs. When geothermal water is simply allowed to stand at constant temperature, pressure, and pH, monomeric silica polymerizes with itself and therefore grows primary particles which are capable of being converted to secondary particles which are further capable of being precipitated. As noted above, after the appropriate amount of primary particles have grown to the appropriate size by aging the

- 36 -

geothermal fluid, precipitation thereof can be facilitated by the addition of an appropriate precipitation agent. However, when this same geothermal water, containing siliceous values which are about to polymerize, is allowed to age in the presence of amorphous silica particles, so that the polymerizing silica now has a receptive surface to grow on, the removal of silica from the liquid phase to the solid phase occurs more rapidly. The induction period which is characteristic of a polymerization/particle growth/precipitation system is substantially shortened, and a different, and quite valuable product is produced.

It has been found that it is possible to cause the polymerized siliceous values in the silica sol to precipitate on to these previously made tertiary aggregate particles and to continue to do so thereon until the appropriate sized particles are produced without the presence of other precipitation agents at this stage. Once the grown particles are of an acceptable dimension, use is made of other said precipitation agents to effect complete precipitation of the tertiary aggregate silica. The particles of amorphous silica made according to this aspect of this invention have substantially reduced contaminant levels, because no additional elements, such as calcium ions, are added in order to cause the growth of the desired particles and the precipitation thereof. Geothermal Type I, II and III silicas precipitated according to this aspect of this invention have low arsenic concentrations as illustrated by analysis shown for process example 1 in Table 1. of course, it is not possible to eliminate all extraneous materials from the product. There are usually some extraneous ions, both cations and anions, in the source fluid which will coprecipitate or be occluded with the silica. Further, there may be some extraneous ions in with the previously prepared silica particles which are being used as the precipitation agent. However, the amount of extraneous materials can be significantly reduced by practising this aspect of this invention.

When using a heterogenous precipitation agent, such as a slurry of previously prepared tertiary aggregate silica particles, it is appropriate to sequentially add or recycle a selected portion of the silica which has already been accepted and recovered from source fluid. It is important to expose the introduced silica particles to an appropriate amount of freshly separated geothermal water; in order to achieve to desired growth in secondary particle

- 37 -

dimension and degree of reinforcement of secondary and tertiary structure to produce certain end product specifications eg. oil absorption capacity. The amount of slurry added and the points at which it is added will alter the range in secondary and tertiary particle size distribution which will result from the process.

- 5 This may be in a single recycle process, cascaded or sequential reactor system, or a continuous flow type reactor, as appropriate.

The sequentially added or recycled particles can still be associated with the fluid in which they are resident without further recovery or purification thereof. Alternatively, the silica particles can be separated from the liquid and stored, and
10 then reslurried for use at a later time. In any case, it has been found to be preferred in the practice of this aspect of this invention, not to add dry silica particles to the geothermal source fluid, but to always add these heterogeneous precipitation agents as a slurry.

It has been found that a small proportion of the heterogeneous
15 precipitation agent is all that is needed to achieve precipitation of primary particles onto pre-existing solid silica surfaces. Suitably about 0.01 to 5.0 weight per cent of silica particles, relative to the weight of the geothermal source fluid being treated, are all that are needed. It is within the scope of this invention to use such heterogeneous precipitation agents alone or in combination with one or
20 more other precipitation/ coagulation aids as aforesaid.

It has been found, quite unexpectedly, that the amorphous silica product made according to this aspect of this invention is somewhat different from the tertiary aggregate particles of amorphous silica which have been made using a coagulation/ precipitation agent according to New Zealand Patent No.
25 232170/228472. It would have been expected that the accreted silica products made according to this aspect of this invention would be larger than the particles from which they were made, because of the additional silica which precipitated on these original particles. Further, it would have been expected that some of the pore volume of the precipitated silica would be reduced by this growth. It has
30 been found, however that, unexpectedly, this larger particle product made by this preferred process has a higher oil absorption capacity and therefore higher pore volume than the smaller particles of amorphous silica which were used as the

- 38 -

precipitation agent. In addition, it has been found that as the secondary particle size is increased up to at least about 30 nm. the opacity or reflectance of the silica product increases to levels above that of commercial silica and calcined clay filler products (see Figure 17)

5 It is noted that the new, larger particles made by this aspect of this invention have a higher wet strength but a lower dry strength than the original precipitated silica used at the outset. The accreted product particles can be easily ground to a readily dispersible, finely divided white powder.

According to this aspect of this embodiment of this invention, particles of
10 tertiary aggregate amorphous silica of suitable Types I, II or III, are formed by the main embodiment of this invention using a cationic or other precipitation/coagulation agent, such as calcium ions. In this step, the calcium ions are added at a point where the monomeric and polymeric silica concentration is close to the equilibrium solubility of the amorphous silica. The equilibrium
15 solubility of the amorphous silica in the geothermal water is defined as the stable molybdate active silica concentration obtained when the geothermal water is maintained at constant temperature and pH, and is not otherwise altered. This yields Type I tertiary aggregate particles with a secondary particles size of about 4 to 10 nm.

20 This tertiary aggregate silica is then admixed with freshly separated geothermal fluid, causing the dissolved and suspended silica, comprising primary particles of the silica in the silica sol of the fresh water, to precipitate on to the tertiary aggregate particles of silica which have been previously made and sequentially added or recycled. By this process, the size of the secondary particles
25 can be grown in a controlled manner to at least about 30 nm.

The amount of the increase in size of the secondary particles has been found to be a function of the ratio of the amount of preformed silica particles to the amount of the silica extractable in the fresh (cooled and aged) geothermal water. In order to maximize the growth on the sequentially added or recycled
30 secondary particles of silica a ratio of about 0.05 to 50 parts by weight of preformed silica particles to silica extractable in the fresh geothermal water should be maintained.

- 39 -

The particles of tertiary aggregate amorphous silica which have been made using a particulate silica precipitation agent can themselves be used to induce further precipitation of the primary particles in fresh geothermal water until the particles have grown to the desired secondary particle dimensions. Thus, the
5 smallest particles are those made using a calcium, or other foreign precipitation agent at the beginning of the process and these are added continuously to the freshly separated source fluid. Growth then occurs by precipitation of silica rich primary particles on to preexisting less silica rich tertiary aggregate particles and the overall proportion of foreign matter decreases, and the purity of the recovered
10 silica tertiary aggregate particles increases. Further, the use of such previously prepared particles of tertiary aggregate silica allows the process to be conveniently carried out in a continuous manner with the simple sequential addition or recycle of a portion of the product to an earlier part of the processing sequence.

15 In addition it has been found that other particles such as CaCO_3 and clay can also act as precipitation agents or substrates onto which primary particles of silica can accrete. In this case the substrate particle is coated with layer upon layer of amorphous silica in the form of primary particles. This approach provides a method for applying a coating of amorphous silica to the surface of particulate
20 material.

Recognizing the positive attributes of using previously prepared particles of silica, or other suitable substrates such as CaCO_3 or clay, as an aid to the precipitation of tertiary aggregate silica from geothermal fluids containing siliceous values, it is also an important aspect of this invention to use this technique to
25 protect processing equipment from the adverse effects of the build up of scale, by the uncontrolled precipitation of silica, and siliceous salts thereon, as a consequence of the geothermal water being cooled and depressurized. Thus, it is possible to protect, *inter alia*, steam/water separators, heat exchangers, piping and other processing equipment used in connection with the recovery of energy
30 from geothermal fluids. It is further possible to protect the reinjection well and the fractures in the formation surrounding it, from unwanted deposition.

In cases where conventional heat recovery equipment cannot otherwise be

- 40 -

operated successfully due to silica deposition it has been found that particles of tertiary aggregate silica, which have previously been made according to the process of this invention, should be added to the geothermal fluid before this fluid passes through the conventional heat recovery equipment. Interestingly, the
5 equilibrium solubility of fixed concentrations of monomeric silica values in geothermal fluid at the same temperature, pressure and pH, are different as a function of the presence in that fluid of silica particles made according to this invention. In the past, as energy was removed from the geothermal fluid, and the siliceous values dissolved therein approached the available surface causing fouling
10 of the insides of the piping and equipment. By reacting the geothermal fluid with previously prepared tertiary aggregate particles of amorphous silica, or other particulate material such as CaCO_3 or clay, the silica does not seem to randomly precipitate on the equipment surfaces, but rather preferably accretes onto these previously prepared particles and causes such particles to grow to a size large
15 enough to precipitate. The silica, however, precipitates as particles rather than as scale, which is a condition which can be handled much more readily than when scale forms on the inside of pipes and the like, and the process must be shut down periodically for clean out of the blocking silica scale. Thus, the walls and other surfaces of the processing equipment are protected in an unexpectedly
20 efficient manner, and the desirable silica values are not lost from the system.

There is a further attribute. Since the tendency to form scale has been eliminated, or at least substantially reduced, by the preaddition of the particles of tertiary aggregate silica, or other substrates such as CaCO_3 or clay, to the geothermal source fluid, it has become possible to allow the geothermal fluid to
25 be flashed at much lower pressures and temperatures without scaling becoming a problem. This allows substantially more energy to be recovered from the geothermal water than was previously possible. Thus, whereas without the practice of this aspect of this invention, it was possible to recover only so much of the energy from the geothermal water so as to avoid silica deposition. It is now
30 possible to recover more energy from the fluid by allowing flashing down to a much lower temperature. Typically this means that the temperature can be reduced to 80°C from significantly higher temperatures which would be required

- 41 -

without silica recovery. Thus, with the practice of this aspect of this invention, it is now possible to extract up to about 25% more power from a given geothermal source fluid, and the solids which are generated by the practice of this aspect of this invention are extracted from the system on a regular basis as a desired
5 product, rather than as environmentally undesirable waste. The economics of the use of geothermal resources to generate power have thus been substantially improved.

As the source fluid has more energy extracted therefrom, by being flashed or conductively cooled to a lower temperature, more of the silica content of this
10 fluid is recoverable therefrom. Thus, when previously prepared particles of tertiary aggregate amorphous silica, or other substrates such as CaCO_3 or clay, are added to the geothermal fluid, and energy recovered therefrom so as to reduce the temperature of the geothermal fluid to less than 100°C , more silica values are recovered from the fluid. When the spent geothermal fluid is then reinjected
15 back into the formation from whence it was produced, the reinjected water has substantially less silica content, and therefore, there is less potential damage to the rock formation by the reinjection of cooled fluid by the consequent deposition of silica on the walls of the wells and the producing formation. Not only has the energy generating efficiency of the use of geothermal water been increased, and
20 the amount of desirable special particulate silica available has been increased, but in addition, the operational constraints of reinjection are reduced which improve overall resource management.

It is preferred to add the heterogeneous precipitation agent as early in the process as possible in order to obtain the maximum beneficial effect of
25 monomeric silica removal from freshly separated geothermal water.

Reference is made to Figures 1 - 8 which show several methods of implementing this aspect of this invention. In referring to these figures of the drawing, the same reference characters will be used to denote common elements of the operation.

30 High pressure, high temperature water 10 is produced from a production well 12 and sent to a conventional high pressure separator where the released steam 16 is used to drive a high pressure turbine 18, with the exhaust steam 20

- 42 -

then being used to drive an intermediate pressure turbine 22. The underflow hot, high pressure water 24 which emerges from the high pressure separator 14 is fed to a secondary flash means 26, from which is produced a steam overhead which is also used to drive the intermediate pressure turbine 22. The underflow 28 from the secondary flash means 26 is the geothermal source fluid to be used in the practice of this invention. This fluid 28 is fed through a silica production facility 30 as has been described above. The silica produced in this facility is the product 32 of this invention, and the lean water 34 produced in this facility is suitably sewerred or reinjected by means of a reinjection well 36 as appropriate. It is considered to be within the scope of this aspect of this invention to feed only a portion of the siliceous water 28 exiting the secondary flash means 26 to the silica recovery portion of this process and to reinject or sewer the rest 46. It is also considered to be within the scope of this aspect of this invention to use only a dual pressure condensing turbine in the use of primary and secondary separated steam such that the use of a high pressure turbine set becomes optional.

As illustrated in Figure 1, according to this aspect of this invention, a portion 38 of the silica bearing slurry produced by the silica production facility 30 is sequentially added or recycled and introduced into the underflow from the high pressure separator 24 before this water is allowed to undergo the secondary flashing operation in the means 26.

It is also considered to be within the scope of this invention as shown in Figure 2, to take a slip stream 42 from the underflow 24 of the high pressure separator, to form the desired heterogeneous precipitation agent from the silica values contained therein, and then to reintroduce such precipitation agent into admixture with the remainder of this underflow 24 with or without a portion 38 of the silica bearing slurry produced by the silica production facility 30. In either case, the slurry 38 and 40 containing particulate silica made according to this invention can, if desired, be sequentially added or recycled back to the high pressure separator 14 via line 44 and the removal of desirable siliceous values initiated at this point in the process.

The silica precipitation agent or substrate of Type-I, Type-II or Type-III structure produced as appropriate from the silica plant 30, in slurry, gel or powder

- 43 -

form, may be optionally sequentially added or recycled in a controlled and desired amount via 38 to the input feed 24 to the secondary separator (Figure 8) or the output flow from the high pressure separator (Figure 5); or via lines 38 and 44 directly to the high pressure separator (Figures 5 and 8).

5 The precipitation agent or substrate may be prepared according to the NZ Patent No. 232170/228472 as Type-I, Type-II or Type-III as appropriate in a separate step identified as the Heteronucleation or Precipitation Agent Preparation step 40 in Figures 5 and 8. This precipitation agent or substrate is prepared from a feed 42 from the output flow 24 from the high pressure
10 separator, and added in a controlled and desired amount back to flow 24 downstream of the takeoff point for flow 42.

A portion of the Type-I, Type-II or Type-III silica product as appropriate from the silica plant 30, in slurry, gel or powder form may be optionally sequentially added or recycled within the silica plant itself 30.

15 The precipitation agent or substrate which is not amorphous silica of Type-I, Type-II or Type-III structure and may be a material other than silica, for example CaCO_3 or clay, may be prepared and/or provided in the separate Heteronucleation or Precipitation Agent Preparation step 40 in Figures 5 and 8. This is introduced to the flow stream 24.

20 The precipitation agent or substrate prepared at either the Silica Plant 30 or the Heteronucleation or Precipitation Agent Preparation step 40, can also be added to flow 28 from the secondary separation stage (Figure 5) optionally before the heat exchanger 52 takeoff point or after this and before the Silica Plant 30 feed point.

25 The secondary particle size of the resulting silica product 32 from the silica plant 30 can be controlled by either the ratio of the amount of precipitated silica introduced to the amount of geothermal feed water to which it is exposed.

The sequential addition or recycle process for each particular case can be operated in either batch or continuous modes of operation accordingly.

30 The silica precipitation agent or substrate may be as a slurry, gel or fine powder.

In the process depicted in Figure 3, the same operation as was described

- 44 -

with relation to Figure 2 is also carried out. The addition in this process is of a separate, downstream process 48 for the recovery of minerals other than silica. Such minerals may be lithium, arsenic or boron containing. It is to be noted that this depicted process allows for the bypass of the additional mineral recovery
5 portion of the operations of this invention, via a line 50, but not the silica removal and sequential addition or recycle operations, and the feeding of the resultant stream to sewer or to reinjection as appropriate.

Figure 4 illustrates the operation of the general process of this invention with the addition of a secondary heat exchanger 52 which may extract heat from
10 all or a portion of the underflow 24 from the high pressure separator. It is to be noted that two conventional means of doing this are a binary cycle electricity generator 54, or a direct heat utilization means 56. The use of these pieces of equipment is made possible by the ability of this invention to reduce downstream operational constraints with respect to silica deposition in the practice of
15 reinjection, and to take much more silica out of the geothermal fluid source and to thereby be able to protect the internals of this equipment from fouling due to uncontrolled silica precipitation. It is to be noted that in this embodiment of this invention, the high pressure turbine 18 is an optional piece of equipment given that only primary separated steam is available. The binary cycle electricity
20 generator or the direct heating operation, or both will employ the additional energy which is resident in the underflow from the high pressure separator.

In the process depicted in Figure 5, the same operation as was described with relation to Figure 4 is also carried out. The addition in this process is of a separate, downstream process 48 for the recovery of minerals other than silica. It
25 is to be noted that this depicted process allows for the bypass of the additional mineral recovery portion of the operations of this invention, via a line 50, but not the silica removal and sequential addition or recycle operations, and the feeding of the resultant stream to sewer or to reinjection as appropriate.

Figure 6 illustrates a process wherein the attributes of the processes of
30 Figures 1 and 3 are combined. Figure 7 shows a process wherein all of the operations shown in Figures 2 and 5 are combined. In addition, an option of sewerage or reinjecting a portion of the spent geothermal fluid before recovering

- 45 -

any additional heat or any silica therefore has been included at 58.

In the process depicted in Figure 8, the same operation as was described with relation to Figure 7 is also carried out. The addition in this process is of a separate, downstream process 48 for the recovery of minerals other than silica. It is to be noted that this depicted process allows for the bypass of the additional mineral recovery portion of the operations of this invention, via a line 50, but not the silica removal and sequential addition or recycle operations, and the feeding of the resultant stream to sewer or to reinjection as appropriate.

Preferably the harvesting of the precipitated tertiary aggregate silica particles is performed using any known separation or purification process. These include: water washing, or other cleaning steps for the particulate product derived from the practice of this invention, or it may simply involve the conventional isolation and recovery of an aqueous slurry of the particles of amorphous silica. The nature of the cleaning and other work up procedures is dependent on the ultimate use which will be made of the products of this invention.

A full schematic diagram of how a continuous process employing silica slurry sequential addition or recycle is operated is shown in Figure 16. This is further illustrated by process example 2 which used plant described in New Zealand Patent No. 232170/228472 to manufacture a high oil absorption silica similar in properties to that shown in Table 1, for silica from Process Example 1 .

PROCESS VARIABLES

Details of the process variables which include cooling, arsenic adsorption, water pH, ageing, precipitation and separation, and the effect of these on the quality and characteristics of the product Type I, II or III silica are presented in New Zealand Patent No. 232170/228472.

A similar consideration of these process variables is also important to the practice of this invention. In addition, for the precipitation step where previously prepared particles of silica are used as the coagulation/precipitation agent, the mechanism is that of templated growth of the dissolved silica onto the surface of

- 46 -

these previously prepared precipitated silica particles. In this use, the acceptable concentrations of the previously prepared silica particles is about 0.1 to 10 grams per kilogram of solution, preferably, about 0.5 to 5 g.kg⁻¹. These previously prepared silica particles should be used in particle sizes of about 5 to 100 nm, preferably up to about 30 nm. Particles of other materials such as CaCO₃ and clay can also be used in similar concentrations as a precipitation agent or substrate onto which the silica is recovered as a surface coating of primary particles of silica.

In one aspect of this invention, it is appropriate to sequentially add or recycle the particles of silica in slurry form. One method of carrying this out is to recover as much particulate silica, from conducting the process of this invention, as possible, since it will be clear that it is not practical to recover all of the silica particles from the aqueous slurry product of this invention, it is considered to be within the scope of this invention to take as much solid product out of the aqueous slurry and to sequentially add or recycle what is left.

A further refinement of this procedure is to separate and recover as much solid particulate product as desired, dewater the remaining dilute slurry, and then sequentially add or recycle the now more concentrated (dewatered) slurry to aid in the growth and precipitation of the desirable particulate product. In this embodiment of this invention, it is appropriate to sequentially add or recycle a slurry having a particulate silica concentration of about 0.5 to 40 weight per cent, preferably about 0.5 to 10 weight per cent.

An attribute of the use of previously prepared silica particles having microstructures of Types I, II or III, as set forth above as all or part of the

- 47 -

precipitation agent is the fact that the use of such materials allow internal portions of operating equipment, such as pipes, heat exchange tubes, etc, to be protected from the indiscriminate deposition of random morphology silica thereon. In contrast to the prior art operations where silica seeding has been
5 used to try to protect the inside surfaces of equipment used in power generation from geothermal fluid, when previously made particles of the special Types I, II or III silica are used, the result is the generation of additional particles of this same microstructure. Thus, in addition to the simple protection of equipment surfaces against fouling, the act of protection is made an integral part of the recovery of a
10 valuable and specifically manufactured product.

The precipitated silica product can be removed as a slurry preferably from a thickener and/or clarifier by clarification, or by filtration. Dissolved air flotation may be used but this would provide an oxidising environment which may be undesirable with regard to arsenic adsorption and corrosion in downstream
15 pipework. If a dry product is required this may be accomplished using for example spray, rotary, belt or tray type driers, followed if necessary, by further milling or grinding to yield a solid product with an appropriate tertiary aggregate particle structure and size range required for particular commercial usage. As drying and milling are important in determining the final particle size and characteristics of
20 the silica product, the particular drying and milling system must be selected with reference to the actual end use application of the silica product. If the geothermal resource is located close to a paper mill, it is within the scope of this invention to pipe the slurry product or a portion thereof, to the mill for incorporation directly into the papermaking process. In this last regard, it is

- 48 -

appropriate to use the slurry in the concentration at which it is produced. It is also appropriate to adjust the concentration of the slurry by either raising or lowering it as needed for the use intended.

The slurry product can be conveniently stored in a covered tank fitted with a submerged agitator. Slurry solids content should be maintained below about 30 kg m⁻³ in the case of Type I silica having an average secondary particle dimension less than about 30 nm. Above this, viscosity rises exponentially and eventually the slurry reaches its gel point. However, adjustment of the solids content of the product is done in a conventional manner to any concentration as required by the use to which this product will be put. Type I slurries wherein the secondary particle dimensions are between 4 - 10nm exhibit thixotropic properties and can impart these to the medium to which they are to be applied. However, for Types II and III silicas, this thixotropic property is far less evident and slurry solids content of up to about 400 kg m⁻³ can be achieved.

15

EXAMPLES OF THE PREPARATION OF SILICAS ACCORDING TO THIS INVENTION

20

The following examples are given to illustrate the instant process for the recovery of tertiary aggregate particles of amorphous silica from geothermal fluid sources. These examples illustrate various process operating conditions, and equipment used to produce several precipitated silica products. The geothermal

- 49 -

water which was used in these examples was derived from the combined flow of production wells KA21 and KA27 situated within the Kawerau Geothermal resource in New Zealand. The results which have been achieved by this invention and are illustrated by these examples have also been achieved with geothermal
5 water from wells in the Kawerau resource (KA19 and 35).

In these examples, parts and percentages are by weight, unless expressly stated to be on some other basis. The following examples of the process of this invention are based on atmospheric discharge from the separators (initially at a temperature of 172°C) which has undergone two processes. Part of the total flow
10 from the separators passed through a binary cycle turbine and was recharged to the main silencer at 110°C. The remainder flowed directly to the main silencer.

**Process Example 1 - Production of Type I Tertiary Aggregate Silica
by Reaction of Precipitated Silica with Freshly
15 Separated Geothermal Water**

A slurry of Type I silica particles, having a secondary particle size of about 6-8 nm, which had been produced by a process according to New Zealand Patent 232170/228472, was placed in a 5 litre beaker, and enough freshly separated
20 geothermal water was admixed with the slurry so that the weight ratio of precipitated silica in the slurry to separated geothermal water was 0.005, or a 0.5 weight percent solids composition. The mixture was then stirred at 1,000 RPM for 30 minutes at a constant temperature of about 90°C. The pH of the mixture remained at 8.5 (90° C).

- 50 -

The mixture produced particulate silica, a portion of which was recovered for characterization, including examination by transmission electron microscopy. It was found that the precipitated particle product was also Type I tertiary aggregate amorphous silica, but this material had a substantially larger particle size than did the precipitated silica added as the substrate.

This procedure was repeated twenty (20) times, using a portion (such that the dry equivalent weight ratio of the precipitated silica slurry to the weight of separated geothermal water was maintained constant at 0.005) of the slurry produced in the preceding batch as the precipitation agent for the next batch.

Figure 9 hereof shows the rate at which monomeric silica is removed from freshly separated geothermal water by reaction by the process of this invention in the presence of previously prepared particles of Type I silica having a secondary particle size of about 6-8 nm. For comparison purposes, this figure also shows the rate at which monomeric silica in the same geothermal source fluid is removed therefrom by natural means at constant temperature and pH by using only naturally occurring polymerization which involves spontaneous or homogeneous nucleation. In this regard, reference is made to the data points indicated for POLY #1 and POLY #2 in this Figure 9 and the curves drawn therethrough to show what happens in the absence of heterogeneous nucleating (precipitation) agents. It will be apparent that these curves show that the decline in concentration of monomeric silica in the geothermal fluid which occurs naturally is quite slow because it is controlled by the amount of particulate silica which is produced by natural, or homogeneous nucleation.

In contrast, the rate of particle formation and of the disappearance of

- 51 -

monomeric silica from the geothermal fluid is significantly higher when there are preformed particles of tertiary aggregate silica admixed with the geothermal source fluid, even in such a small amount as 0.5 weight percent. In the curves shown in Figure 9, the first measurement of the monomeric silica content of the water was at four (4) minutes into the run. The monomeric silica concentrations for the heteronucleated system in run #1 were about 160 mg.kg⁻¹ less than in the geothermal fluid which had no precipitated silica added.

After 30 minutes of contact and aging, a portion of the silica particle slurry of run #1 was used in the same manner to be admixed with the same amount of the same freshly separated geothermal source fluid. This same procedure was repeated twenty times (the analysis of the first ten times indicated in Figure 9), with the slurry of the previous run being used in the next subsequent run. In the second run, the concentration of monomeric silica in the source fluid declined about 300 mg.kg⁻¹ after four (4) minutes of contact. The particulate silica recovered from some of these runs was examined by transmission electron microscopy (Figures 10 - 14) and found to be substantially the same as the particles which had been sequentially added or recycled, except that the secondary particle size of these particles was substantially larger. The growth of the secondary particles was measured at runs 5,, 10, 15 and 20 and is described by the graph shown in Figure 15. The typical increase in spectral reflectance with increased secondary particle size is shown in Figure 17.

- 52 -

**by Reaction of Precipitated Silica with Freshly
Separated Geothermal Water**

A process including continuous sequential addition or recycle of Type I silica was operated according to parameters depicted in schematic form in Figure 5 16. Separated water of pH 8.67 - 8.71 (80°C) with a flow rate of 4.5 kg.s⁻¹ and a silica concentration of 742 mg.kg⁻¹ was flash cooled to 80°C. To this water 0.14 kg.s⁻¹ of Type I silica slurry of 2 wt% consistency and having secondary particle dimensions from 6 to 10 nm was admixed in a precipitator vessel for up to about 10 5 minutes. Magnafloc 368 and Polyethylene Oxide (6 million molecular weight) were added such that the equivalent solution concentration of these were 1 mg.kg⁻¹ and 1 mg.kg⁻¹ respectively. Final flocculation and settling was achieved in the clarifier depicted in Figure 14 of New Zealand Patent 232170/228472. Recovery of the silica and further reaction with freshly separated source geothermal water 15 was continued until the secondary particle dimension of the harvested silica had increased to a mean of 13 nm. The chemical characteristics of this precipitate after washing were very similar to that reported for the precipitate from process example 1, shown in Table 1.

Chemical and physical characteristics of these precipitated silicas are 20 discussed below. The important physical and chemical parameters which characterize the suite of precipitated silicas made according to this invention are hereafter illustrated.

Physical and Chemical Characterization of Silica Products of the Process

- 53 -

Physical and chemical characteristics are discussed for examples of silica products made in the laboratory and on a pilot plant continuous scale according to this invention, to illustrate:

- i) the properties of precipitated silicas produced under process conditions outlined in the process examples hereof; and
- ii) the influence of process variables on the chemical composition, and also on the physical and structural characteristics of the products of this invention.

10

Type I Silicas Produced by Reaction of Precipitated Silica with Freshly Separated Geothermal Water

Characterization

15 The starting silica particles used in process example 1 above had a secondary particle size of about 6.5 - 10.5 nm. The average pore diameter of these starting particles was about 7 nm, as determined by interpretation of absorption-desorption isotherms using nitrogen as the adsorbed species. Table 1 below shows the chemical and the physical properties of Type I particulate silicas made according to New Zealand Patent 232170/228472. Most importantly Figures 10-14 (which are TEM micrographs all of the same magnification) show the progressive growth of Type I silica when this is repeatedly exposed to freshly separated geothermal water. It is also apparent from these micrographs that the silica which has been removed from solution possesses the same fundamental

20

- 54 -

structure being that of the primary particle and that the overall Type I structure has been maintained as growth has occurred.

The surface area and oil absorption analyses for the initial starting Type I silica and this same silica after runs 10, 15, and 20 are shown in Table 2. A significant increase in oil absorption capacity occurred as secondary particle dimensions increased above 15nm and the oil absorption capacity appeared to reach a maximum from 20 - 30 nm. The spectral reflectance also increased with increasing secondary particle size (eg. see Figure 17).

10

- 55 -

TABLE 1. Physical and Chemical Properties of Geothermal Silicas

Physical Properties									
5	SILICA	Secondary Part. Size (nm)		Tertiary Part. Size (% , 1 μm)		BET Surface Area (m ² g ⁻¹)		Oil Absorption (g 100g ⁻¹)	Dry Strength (hand grind)
	TYPE I (Example 1 - NZ Pat. No.232170/228472)	6-8		0		120		130	Brittle
10	TYPE II (Process Example 1)	29		75		55		209	very soft friable
Chemical Properties (Unwashed)									
15	SILICA	SiO ₂ (%)	Al ₂ (%)	O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	Na ₂ O (%)	K ₂ O (ppm)	As LOI (%)
20	TYPE I (Example 1 - NZ Pat. No. 232170/228472)	76.93	0.33	0.02	7.23	1.14	0.28	38.6	13.94
25	TYPE I (Process Example 1)	86.22	0.68	0.06	3.95	0.44	0.26	7.4	8.66
Chemical Properties (Washed)									
30	TYPE I (Process Example 1)	92.90	0.28	0.03	0.33	0.11	0.14	<5.0	5.67
35									

TABLE 2. PHYSICAL PROPERTIES OF RECYCLED TYPE I SILICAS

	RUN NUMBER	TEM SECONDARY PARTICLE SIZE	BET SURFACE AREA	OIL ABSORPTION CAPACITY
		nm	$m^2 g^{-1}$	$g 100g^{-1}$
40	INITIAL SILICA	8.4	149	126
	RUN # 10	18.4	84	173
	RUN # 15	25.8	56	223
	RUN # 20	28.7	49	209

- 56 -

PRODUCT APPLICATIONS

The precipitated amorphous silicas identified herein, particularly those in which the silica has been recovered onto an amorphous silica precipitation agent or substrate, can be obtained directly in a high purity at greater than 99 wt%

5 SiO_2 , on an anhydrous basis, with relative ease. This product can be further upgraded by washing the adsorbed calcium from the surface of the initial silica precipitation agent or substrate, prior to the recovery of further silica. The final product may also be washed to remove any other surface contaminants.

The optical properties, when measured on a silica product made according
10 to this invention, can have the following L^* , a^* and b^* values (CIE scale, illuminant D65, and 10° viewing angle from normal observer): $L^* = 97.8$; $a^* = 0.0$; $b^* = 1.3$

Type I silica made according to this invention whereby the calcium, which is used as the precipitation agent, is added to the geothermal water after only a
15 short ageing time yields a product with a particle size of about 12 nm. which is slightly larger than that of about 7 nm. produced when the calcium is added after ageing is essentially complete. With this larger secondary particle size the bridging structure of the Type I silica is stronger and the pore structure does not collapse on drying the product from a slurry. This attribute is important when the silica is
20 added to paper as a filler to reduce print through by absorbing the oil associated with the printing ink into the pores of the silica, thereby restricting the passage of oil through the paper (example 3).

If however the silica is prepared according to the aspect of this invention whereby the silica is recovered from the water onto a Type I silica precipitation
25 agent or substrate, and the secondary particle size is increased to about 20-25 nm. using sequential addition or recycle, as in process examples 2 and 4, there is a corresponding increase in the oil absorption and also in light scattering properties of the silica (eg. see Figure 17). This complementary increase in both these properties is a unique feature of these silica products, and makes them ideally
30 suitable as high performance fillers in paper to enhance both the optical properties of the paper (unprinted opacity and brightness) and also reduce print through (enhance the printed opacity). Silica has been prepared according to this

- 57 -

aspect of the invention, added to newsprint on a commercial scale, and the resulting paper printed commercially, yielding results which are significantly better than those achievably using other commercially available silica products (Example 4, Table 4).

5 The unique combination of high oil absorption and enhanced light scattering properties of Type I silica with a larger secondary particle size, prepared according to this invention utilising sequential addition or recycle, also enable this silica to be used for paper coating, particularly for ink jet type printer papers where both opacity and high and rapid ink absorption are important
10 requirements (Examples 4 and 5).

In addition the enhanced light scattering properties make this silica ideally suitable as an additive to paint formulations, where it functions more effectively in providing opacity and as an extender for titanium dioxide, than other commercial silica products used for this purpose.

15 The relatively high surface area of Types I and III silicas, made according to this invention, their complex structural characteristics, and their high pore volumes, make these silicas suitable for many applications where the absorptive capacity of additives is important. These silicas are often used as inert carriers for agricultural and other products.

20 Durable rubber products generally require the use of a filler with an open reticulated structure. Such fillers are required to have surface areas of about $160 \text{ m}^2\text{g}^{-1}$ and oil absorption capacities of about 210 g.100 g^{-1} . The silica product detailed in example 9 which has been prepared according to this invention, with a secondary particle size of about 13 nm and a surface area and oil absorption
25 consistent with these requirements, is ideally suited as a high performance filler in rubber (Example 6, Table 5).

Silicas which are normally made synthetically under anhydrous conditions and using very high energy processes are similar to the Type II silicas of this invention. These silicas do not have the same thixotropic qualities as the Type I
30 silica tertiary aggregate particles hereof. Type II silicas are easily dispersed in most solid and liquid systems and have good light scattering properties. They are can be used as extenders in systems which conventionally employ expensive high

- 58 -

grade opacifying fillers or coatings, e.g. TiO_2

APPLICATION AS A PAPER FILLER AND IN PAPER COATING

In yet a further aspect, the present invention consists of paper filled with, and/or coated with precipitated amorphous silica derived from a process of the present invention. In filling paper with the silica particles of this invention, it is appropriate to add the silica to the pulp prior to conversion of the pulp into the paper by the conventional wire draining processes or the like. In some cases, it might be appropriate to add the silica during the pulp mixing operation which precedes paper formation. In the alternative, it is possible to add the silica at the very end of the pulp mixing portion of the paper making process. The silica for this use may be put up in either a slurry or a powder form. If the silica is in the slurry form, the amount of water in the silica slurry should be taken into account when calculating the amount of slurry needed to achieve a target silica filler content in the paper.

It is also within the scope of this invention to apply the silica of this invention as a coating onto an already formed paper sheet. In this embodiment of this invention, it is appropriate to provide the silica as a slurry, and then to use conventional coating techniques to apply the silica slurry to the surface of the paper. Such techniques include spraying, applying with a doctor blade, and the like. It would be appropriate to apply the silica coating by dipping the paper in the slurry, whilst taking precautions to insure that contact of the paper with the water in the slurry does not disrupt the paper.

As a filler, the amount of silica should be controlled, relative to the paper weight, to be about 0.5 to 20 weight percent, preferably about 1 to 5 weight percent. In these proportions, it has been found that the opacity of the paper is substantially improved as compared to the opacity of the same paper which has been filled with the same amount of conventionally derived silica. Further, when used as a filler in these proportions, it has been found that the ultimate paper product has substantially improved ink retention, that is the ability to hold ink in the place where it has been printed without it either running away from the printed areas or bleeding through the paper to the other side thereof. This results

- 59 -

in substantially reduced print through. In addition there is an increase in both the brightness and opacity of the unprinted sheet

As a coating, the silica should be applied in such proportions that the coated weight of silica in the product is about 3 to 30g.m⁻². The coating weight is preferably about 15 to 20g.m⁻². When the silicas of this invention are coated onto the previously formed paper according to this aspect of this invention, the product has substantially improved whiteness and opacity, as compared to the same paper coated with the same proportion of conventional silica. It also has substantially improved ink receptivity and ink location retention.

It appears that the silicas of this invention have a unique micro-structure which is well suited to receiving, absorbing, and holding the ink particles on its surface. This causes the ink to remain on the surface of and in the location on that surface where it is printed. Of course this is a very desirable attribute of the silicas of this invention. This makes the silica product particularly attractive for coating ink jet type printer paper where high localised ink retention and good opacity are important requirements.

A precipitated silica slurry made according to the process of this invention can be used directly in the paper-making process, where it is incorporated into the paper sheet to improve print and optical qualities. Alternatively, if the product is recovered from the processes of this invention as a dry solid, it may be re-slurried and then used similarly.

PAPER FILLING

Precipitated silica products described herein have been tested as fillers in paper handsheets and also in paper made on a paper machine under commercial production conditions, and printed in the laboratory and in commercial pressrooms using letterpress and offset printing presses. The optical and print quality of the paper filled with various silicas made according to this invention have been tested and compared to those papers filled similarly with other commercially available high grade fillers.

Handsheets were manufactured using a typical newsprint pulp having a strict grammage tolerance of 48 +/- 0.5 g m⁻² (air dry weight - AD). These were

- 60 -

then soft calendered to a caliper of $75 \pm 3 \mu\text{m}$ to obtain a representative sheet for comparison with industry standard newsprint.

In the examples where Type I tertiary aggregate amorphous silica, prepared according to this invention in which sequential addition or recycle is used to increase the secondary particle size to about 20-25 nm, was used in combination with paper, print-through decreased by as much as 0.07 units at a filler content of 2.2 wt %. Opacity was increased by as much as 4 percentage points at this 2.2 wt % addition. Both wire and felt sides of the paper were similarly improved at the two (2) inking levels tested (Print Densities PD=0.85 and PD=1.00).

The following examples show the addition to paper of the silica derived from geothermal fluid sources according to this invention. The silica particles of this invention were added to virgin newsprint fibre and the mixture converted into paper in the conventional commercial manner. The properties of the printed and the unprinted newsprint were examined and compared to similar papers prepared with no fillers or other fillers as will be apparent. In these examples, parts and percentages are by weight unless expressly stated to be on some other basis.

EXAMPLE 3

Ten (10) tons of dry equivalent Type I silica was extracted from geothermal water discharged from wells KA21 and KA27 at the Kawerau geothermal resource from a process similar to that set forth in Example 1 of New Zealand Patent No. 232170/228472. Calcium was used as the precipitation agent and this was added to the water prior to the completion of the ageing period, to yield a Type I silica product with a mean secondary particle size of 12 nm. No sequential addition or recycle was used. The silica product was put up in a 5 weight per cent slurry, and then transported to storage chests proximate to a paper making machine. This silica had a BET surface area of $53\text{m}^2.\text{g}^{-1}$, an oil absorption capacity of $130\text{ g } 100\text{ g}^{-1}$, and a reflectance of 95.2% at 550 nm (D65/10° from normal observer).

The slurry of silica was pumped into the paper machine headbox overflow to the machine chest such that it returned to the headbox and then directly to the

- 61 -

paper machine via the primary and the secondary fan pumps. The flow rate of the silica slurry was adjusted such that the target concentration of 1.5 weight percent silica in air dry paper was achieved.

Table 2, below reports the significant physical properties of the newsprint sheet produced from this run in the paper making machine. It will be clear from the data in the table that separate trials were conducted during which the same newsprint was filled with: geothermal silica made according to this invention; calcined clay; and no filler at all. The wood supply, bleaching program and pulp components supplied to the machine at the time of the trials were the same. It was possible to examine the unprinted and the printed properties of the filled and unfilled sheets produced from the same machine.

The paper was tested for unprinted properties according to methods specified by TAPPI (1987). Printed properties, such as "print through", were assessed in the laboratory using an IGT laboratory press and commercially on letterpress and offset presses. The initial commercial press room trials were conducted separately for the samples filled with the geothermal silica and the calcined clay, respectively.

TABLE 2. NEW IMPROVEMENT WITH ADDITION OF GEOTHERMAL SILICA

	Property of 48.8 g.m ⁻² Standard Newsprint	Geothermal Silica (1.8 wt%)	Calcined Clay (1.7 wt%)
25	Brightness (points)	+1.7	+1.4
	Opacity (points)	+1.7	+1.1
30	L* (points)	+0.9	+0.8
	Porosity	+15%	0%
	Top Side Roughness	-10%	0%
35	Burst Strength	-10%	-9%
	Tensile Strength	-6%	0%
40	Coefficient of Friction	+14%	Not Measured
	Print Through Reduction Offset Press	25-30% 1.5 wt% silica	20% 1.7 wt% clay
45	Print Through Reduction Letterpress Press	15-20% 1.5 wt% silica	10% 1.7 % clay

- 62 -

Both filled samples were run simultaneously with the unfilled paper on the same press such that a direct comparison could be made with respect to the unfilled sheet before and after the same newsprint edition to remove any possibility that the unfilled sheet in the above comparison had contributed to the differences in the performance of the two fillers.

The results of these tests are shown in Table 3, below.

**TABLE 3. COMMERCIAL PRINTING OF GEOTHERMAL SILICA
FILLED NEWSPRINT**

Offset Press	Print-through	%Reduction
Unfilled 48.8 g m ⁻²	0.056	-
Geothermal Silica 1.5 wt%; 48.8 g m ⁻²	0.040	28.6
Calcined Clay 1.7 wt%; 48.8 g m ⁻²	0.044	19.6
Letterpress Press	Print-through	%Reduction
Unfilled	0.070	-
Geothermal Silica 1.5 wt%; 48.8 g m ⁻²	0.061	+13
Calcined Clay 1.7 wt%; 48.8 g m ⁻²	0.075	-7

It should be noted that the increase in opacity and brightness of 1.7 points at 1.8% geothermal silica in the paper was far above expectations in comparison with the performance of the calcined clay, which is a material which is specially manufactured to effect improvements in the opacity and brightness of newsprint,

- 63 -

at low ash levels. The commercial print through measurements indicated that twice as much calcined clay would have been required in this particular tested sample of newsprint to achieve the same print quality.

Commercial synthetic silicas and silicates are already used as fillers in the paper industry. The principal reason for using silicas as fillers is to improve the oil absorption capacity of the filled paper sheet such that the print does not show through so much from one side to the reverse side. The expectations of the paper maker, with respect to the improvement in opacity as compared to that achievable with commercial silicas, was low. When commercially available silicas are added to newsprint stock at a loading of about 1.5 to 3.0 weight percent, the opacity increases are quite small as compared to the same unfilled paper. In fact, in 1985, Bown (paper entitled: "Fillers for Uncoated Groundwood Papers; Proc. 2nd Uncoated Groundwood Papers Conference, New York) documented these changes in opacity as being insignificant.

In contrast to this report of insignificant increases in opacity brought about by the use of commercially available silica fillers, as shown in Table 4, for 48.8 g.m⁻² standard newsprint, the increase in opacity brought about by using the special silicas of this invention as fillers was not only significant, it was even slightly better than the opacity increase which was achievable by the use of the specially designed calcined clays which are the standard in the industry. Further, these data also show that the reduction in print through was significant, and was significantly better than with the conventional calcined clay.

EXAMPLE 4

In the above Example 3, the mean particle dimension of the secondary particles of the Type I silica was about 12 nm, which is somewhat smaller than the particle sizes of the commercial, synthetically manufactured silicas which have been used in the newsprint industry. These commercial silicas have been analyzed by TEM as having particle sizes of about 15-25 nm. As laboratory work had shown that both the oil absorption and light scattering (reflectance) (Figure 17) of the Type I silica increased with increasing secondary particle size up to about 30 nm., it was decided to take advantage of this unique combination of properties and use this silica as a filler in paper. About six tonnes of Type I silica was manufactured according to this invention, utilising a Type I silica as a precipitation agent or substrate to obtain growth by a recycle operation to increase the mean secondary particle size to about 26 nm. (Figure 13). The oil absorption capacity of this silica was 223 g 100 g⁻¹ (determined by the spatula rub out method using boiled linseed oil). The particle size analysis of the powder, by laser using a Malvern Mastersizer, showed that 75% of the particles had a dimension of less than 1 μ m.

For this, geothermal water at about 98°C, containing an average of 762 mg.kg⁻¹ dissolved silica was taken from the weirbox water from the KA21, KA27 and KA36 wells of the Kawerau geothermal field. A Type I silica for use as a precipitation agent or substrate was prepared according to New Zealand Patent No. 232170/228472 with the water being aged at 55°C and calcium used as the coagulant. The silica was prepared in a continuous process using an input flow of

- 65 -

geothermal water at about 8 litres per second. Following ageing in the conditioning vessels and subsequent precipitation of the silica, the geothermal water with the precipitated silica was pumped to a clarifier vessel where the particulate silica was allowed to settle and the residual geothermal water drained
5 off the top of the vessel in a continuous manner. In this way a slurry of Type I silica with a consistency of about 2 wt % was formed continuously in the bottom of the clarifier and pumped to a nearby storage tank. About 2.5 tonnes (on an anhydrous silica basis) of silica slurry were produced.

This Type I silica slurry was used as the precipitation agent or substrate
10 onto which further silica was recovered from geothermal water using a semi continuous sequential addition or recycle operation. For the first recycle this slurry was added to a stream of fresh geothermal water which had first been cooled to about 80°C. The mixture was then reacted for a mean residence time of about 10 minutes (the spread of residence times was 7 to 16 minutes), whereupon the
15 dissolved silica in the geothermal feed water was recovered onto the silica substrate, thereby increasing the secondary particle size. A precipitation agent or substrate loading of about 1 gram of silica slurry per litre of aged geothermal water was used. The particulate silica and geothermal water were then pumped to the clarifier vessel where the silica settled as a slurry which was continuously
20 removed by pumping to a storage tank in a similar manner as that described above. Polyethylene Oxide and Magnafloc 368 were used, each at a concentration of 1 mg kg⁻¹, to aid recovery and settling of the particulate silica product as a concentrated slurry.

The separated slurry was then sequentially added or recycled where it was

- 66 -

introduced similarly into a fresh geothermal water stream, from which the dissolved silica was recovered similarly onto the particulate Type I silica substrate, further increasing the secondary particle size. The silica product was again recovered as a concentrated slurry and pumped from the clarifier vessel to the storage tank. After each sequential addition or recycle the secondary particle size was measured from TEM photographs and the oil absorption measured. The sequential addition or recycle process was carried out five times after which the secondary particle size of the Type I silica product had increased to 25 nm. and the oil absorption had increased to 230 g 100g⁻¹. During the sequential addition or recycle process the consistency of the separated silica slurry increased to about 6 wt %. The mean particle size of the silica flocs in the final slurry was about 15 microns. About 6 tonnes (on an anhydrous silica basis) of this Type I silica with these properties, were produced. This final silica slurry was transported by tanker to the storage tanks of the filler addition system of the paper mill.

The silica was used to fill light weight yellow directory grade paper of a basis weight of 38 gsm. The silica slurry was pumped into the machine headbox overflow of the paper machine chest such that it returned to the headbox and then directly to the paper machine via the secondary fan pumps. The slurry flow rate was ramped up slowly over a period of several hours until the target filler concentration of 2.2 wt % silica in air dry paper was achieved.

The paper was tested for unprinted properties and print through in the laboratory at print densities of 1.00 and 0.85, and in a commercial four colour offset press.

In order to provide an objective assessment of the performance of the

- 67 -

geothermal silica product as a paper filler, a similar paper directory grade paper was produced in which the filler (added to a level of 2.6 wt %) was a commercial silica-based product, designed and marketed specifically as a filler for paper to reduce print through and enhance the print and optical properties of the paper.

5 In addition standard unfilled directory grade paper was produced.

The results which are presented in Table 4 below, clearly show that the Geothermal Type I silica with the increased secondary particle size and higher oil absorption produced a substantial reduction (improvement) in print through and also increased the unprinted opacity and brightness of the paper, with respect to
10 the unfilled paper. These improvements were also significantly better than those achieved with the commercial filler. The results therefore confirm the unique and superior performance as a paper filler, of this Type I silica product, made according to this invention in which Type I silica with a small secondary particle size is used as a precipitation agent or substrate onto which dissolved silica is
15 recovered, using a process of sequential addition or recycle, to increase the secondary particle size and pore volume (oil absorption). Indeed the unique combination of increased light scattering and oil absorption properties contribute to the superior performance of this Type I silica product, relative to other high oil absorption capacity commercial synthetic silicas which have been similarly
20 tested.

- 68 -

**TABLE 4 - LABORATORY PRINT THROUGH RESULTS FOR TYPE I
SILICA AND A COMMERCIAL SILICA-BASED FILLER IN YELLOW
DIRECTORY GRADE PAPER**

5

Print Density - 1.00

	Geo Silica	Comm. Silica
Unfilled Print Through	0.182	0.164
Silica Loading	2.2 wt %	2.6 wt %
10 Silica Filled Print	0.111	0.120
Through		
Absolute Improvement	0.071	0.042
% Improvement	39%	21%

15 **Print Density - 0.85**

	Geo Silica	Comm. Silica
Unfilled Print Through	0.138	0.124
Silica Loading	2.2 wt %	2.6 wt %
Silica Filled Print	0.076	0.086
20 Through		
Absolute Improvement	0.062	0.038
% Improvement	45%	31%

PAPER COATING

EXAMPLE 5

Geothermal silica produced by the process set forth in Example 4
5 hereinabove, was added as a component of a coating formulation intended for use
as a paper coating. The silica was intended to function as an inert extender for
the coating, and also to improve the opacity of the coated paper. In this respect,
it was intended that the silica would replace the calcium carbonate, clay or
calcined clay which are conventionally used for these purposes. Because of the
10 increased light scattering properties, the silica is able to contribute more
effectively to the opacity of the coating than do calcined clays or calcium
carbonate, and can therefore be used as an extender for titanium dioxide which is
the main, and costly, component of the coating that specifically provides the
required opacity.

15 The Type I silica used in this example had an average secondary particle
size of about 25 nm, an oil absorption of about 230 g.100 g⁻¹, and a reflectance of
greater than 95% at 550 nm (D65/10' from normal observer). It is added to the
coating composition in a proportion of about 15% of the coating weight. The
coating provides significantly greater opacifying effect than those containing only
20 clay or calcium carbonate, which are conventionally used for this purpose in such
coating formulations. The TAPPI opacity is improved by up to about 3 points,
and the TAPPI brightness is improved by up to 3 points relative to the opacity
and brightness imparted by conventional clays or carbonate.

- 70 -

APPLICATION TO RUBBER

Silicas have been used as reinforcing agents in vulcanized rubbers for many years. The added silica achieves some improvement in the tensile strength, the tear strength, and the elongation prior to break, of rubbers, relative to these same properties in rubbers which have been filled with other materials, such as for example, carbon blacks.

EXAMPLE 6

Type I silica made according to this invention and having the properties set forth in the following Table 5, was added to natural rubber in a proportion of about 60 parts by weight of silica per 100 parts by weight of rubber.

TABLE 5. Properties of Silica Reinforcing Agent

	Surface Area (BET) (m ² /g ⁻¹)	Oil* Absorption (g 100g ⁻¹)	pH 5 wt% aqueous suspension	Tapped Bulk Density (g/cm ⁻³)	TEM cross- section dimension (nm)
Sample 2	155	212	6.3	0.27	13

* - boiled linseed oil; spatula rub-out method

By comparison to the tensile strength, (shore) hardness and tear strength of the same rubber filled with the same amount of conventional silica, the rubber filled according to this invention had unexpected improvements in these properties.

- 71 -

APPLICATION TO CEMENT**EXAMPLE 7**

A sample of geothermal silica manufactured according to Example 3 of hereinabove, was added as a dry powder to concrete mixes comprising normal portland cement and aggregate. Three (3) mixes were made up containing, in place of a comparable amount of the cement: 0% silica; 5% silica and 7% silica, respectively. The water:cement+silica ratio was adjusted to 0.5. All of these mixes were tested according to ISO standard procedures.

The pozzolanic activity of the geothermal silica was demonstrated by its ability to enhance the compressive strength of the concrete relative to the compressive strength of concretes after 7 and 28 days of aging. By comparison, conventional silicas made according to common commercial practice did not substantially change the compressive strength of concrete containing such as compared to unfilled concrete. The following Table 6 shows the compressive strength of the concretes made according to this invention.

TABLE 6. Silica Filler for Concrete

Extent of Cement Replacement By Geothermal Silica	% Increase in Compressive Strength Relative to Standard Concrete	
	<u>7 Day</u>	<u>28 Day</u>
5 wt%	10.0	12.0
7 wt%	14.5	14.0

EXAMPLE 8

In addition a further sample of silica was prepared in a similar manner to that in example 3 hereinabove, where the calcium precipitation agent was added
5 at the commencement of the ageing period. Geothermal water at 100°C containing 770 mg.kg⁻¹ dissolved silica was taken from the KA21/27 weirbox and 200 mg.kg⁻¹ Ca²⁺ was added immediately. The mixture was stirred for 10 minutes wherein flocs of silica with a Type I tertiary structure formed. The secondary particle size was about 12 nm. After this time 1 mg.kg⁻¹ polyethylene oxide and 1
10 mg.kg⁻¹ magnafloc 368 were added to cause the silica flocs to settle as a slurry, which was then dewatered by decantation. The slurry was washed two times by decantation washing using demineralised water, and then two further times using demineralised water in which the pH was adjusted to 6. The purpose of the washing was to remove as much surface adsorbed Ca²⁺ as possible to enable
15 further silica to recovered onto an essentially silica surface of this substrate.

The resulting slurry of washed amorphous silica with a Type I tertiary structure was then used as a precipitation agent or substrate, which was exposed to fresh geothermal water at 100°C using a ratio of about 3 g slurry per liter of water. The reaction was carried out for a period of about 20 minutes wherein the
20 dissolved silica in the geothermal water was recovered onto the Type I silica of the said substrate, thereby increasing the secondary particle size of the Type I silica substrate. The particulate silica product was flocced using 1 mg.kg⁻¹ polyethylene oxide and 1 mg.kg⁻¹ magnafloc 368, and allowed to settle. The supernatant water was removed by decantation to provide a second slurry of silica

- 73 -

of Type I structure with a slightly larger secondary particle size, which was then exposed to a further volume of fresh geothermal water and the above sequence of operations repeated. This sequential addition or recycle process was repeated for a total of 20 times. The final slurry was dried and ground to a fine powder. Using
5 this process the secondary particle size was increased to 18 nm. and the oil absorption of the product increased to 208 g.100g⁻¹.

This silica product, when added to a cement/concrete mix in a similar manner to that detailed in example 7 above is able to increase the compressive strength of the concrete, relative to standard concrete, and to also enhance the
10 rate of increase in the compressive strength.

APPLICATION TO PAINT

EXAMPLE 9

15 Geothermal silica made according to Example 4 hereinabove was added to a paint formulation in order to provide opacity and act as an inert extender or partial replacement of titanium dioxide. The increased light scattering properties of this geothermal silica compared to that of commercial silicas or calcined clays enable the geothermal silica to function more effectively as an extender for
20 titanium dioxide, when added to an otherwise conventional paint formulation in an amount of about 15% by weight.

EXAMPLE 10

Geothermal silica made according to Example 8 hereinabove was added to

- 74 -

a paint formulation in order to act as an inert extender as well as a flattening agent. When added to an otherwise conventional paint formulation in an amount of about 10% by weight, it functions both as an inert extender and an opacifier in the paint. As with example 9 the opacifying effect is significantly better than that
5 which could be achieved with calcined or uncalcined clay, which are known materials for use in this service.

EXAMPLE 11

Geothermal silica made according to this invention was added to a paint
10 formulation in order to act as a flattening agent. The silica was of Type I and had a secondary particle size of about 18 nm. It had an oil absorption of about 150 g 100 g⁻¹ and a reflectance of about 95% at 550 nm (D65/100 from normal). When added to an otherwise conventional paint formulation in an amount of about 10% by weight, it functions effectively as a flattening agent.

- 75 -

CLAIMS:

1. In a process where a fluid is derived from an underground source, said fluid being extracted or extractable from the underground source as a hot high pressure geothermal source fluid having dissolved siliceous values therein and said geothermal source fluid is processed by the following steps A1 and A2:

A1 - first flashing the hot, high pressure geothermal source fluid to a lower pressure and temperature to produce steam and to form a second fluid which is at a lower pressure and temperature, or causing a multiplicity of flashes and/or heat exchange to produce second fluid(s) which is or are at a lower pressure and temperature, and which has or have a higher effective concentration of siliceous values dissolved therein, said steam being vented, used in a heat exchanger and/or used in a turbine or turbines; and

A2 - recovering particles of tertiary aggregate amorphous silica from said second fluid(s) by a process which comprises:

- i) whether by parameters of step A1 and/or otherwise, ensuring the relative amounts of said siliceous values and any precipitation agent contained in said second fluid(s) are insufficient to cause substantial quantities of said siliceous materials to come out of solution in said second fluid(s);
- ii) adjusting to and/or maintaining the pH of said second fluid(s) up to about 9.5 during at least the following sequential steps (iii), (iv) and (v);
- iii) forming a silica sol by causing (whether by step A1 and/or otherwise) or having allowed said second fluid(s) to become supersaturated

- 76 -

with respect to amorphous silica and initiating polymerisation of said siliceous values therein into polymeric material comprising primary particles of polymeric amorphous silica without causing substantial quantities of said siliceous values, including polymers thereof, to
5 independently precipitate;

iv) ageing said silica sol, by holding such for a time and under conditions sufficient to cause and/or to continue polymerisation of said siliceous materials in said sol into said polymeric material and into larger particles thereof, without causing substantial quantities of said polymeric
10 material and/or said particles to independently precipitate;

v) adding to said silica sol a sufficient quantity of at least one precipitation agent to provide a sufficient proportion thereof, in relation to said polymeric and particulate material, to convert said polymeric material and said particles into silica particles having a tertiary aggregate structure
15 of Type-I, Type-II or Type-III, of an amount sufficient to cause rapid precipitation thereof from said silica sol, thereby precipitating at least some of said tertiary aggregate amorphous silica particles to form a slurry of said particles; and

vi) separating said slurry into at least a first portion (which may still
20 include water) comprising said particles and a second portion comprising a more dilute aqueous medium,

a process ensuring a reduction of the amount of siliceous material which precipitates or deposits out of said geothermal source fluid and/or any fraction thereof on to internal surfaces of apparatus (including piping or channels) used to

- 77 -

carry out the process of steps A1 and A2 or at least step A2, which process comprises:

(I) introducing into the second fluid(s) in an amount that until step A2(v) is reached does not lead to any substantial independent precipitation, quantities of
5 silica particles having the tertiary aggregate structure of said Type-I, Type-II or Type-III to be subsequently precipitated out by step A2(v) in a quantity and of a size of particle whereby dissolved siliceous materials in said second geothermal fluid(s) accrete to said added particles but do not substantially precipitate out on to the internal surfaces of said apparatus (including any piping or channels),
10 thereby at least reducing the amount of siliceous values adhering to said apparatus (including any piping or channels) as well as enlarging said added particles of tertiary aggregate amorphous silica of the particular form (Type-I, Type-II or Type-III) added and subsequently with step A2(vi), after the addition of said at least one precipitation agent (which may comprise or include still additional
15 quantities of silica particles of the desired tertiary aggregate structure) recovering said grown added particles of tertiary aggregate amorphous silica of the particular Type-I, Type-II or Type-III;

(II) introducing into the second fluid(s) in an amount that until step A2(v) is reached does not lead to any substantial independent precipitation, quantities of
20 reactive or substrate particles in a quantity and of a size of particle whereby dissolved siliceous materials in said second geothermal fluid(s) accrete to said added particles but do not substantially precipitate out onto the internal surfaces of said apparatus (including any piping or channels) thereby at least reducing the amount of siliceous values adhering to said apparatus (including any piping or

- 78 -

channels) as well as enlarging said added particles by the addition of amorphous silica thereto and subsequently with step A2(vi) after the addition of at least one precipitation agent (which may comprise or include quantities of silica particles of the desired tertiary aggregate structure Type-I, Type-II or Type-III) recovering

5 said grown particles; or

(III) introducing into the second fluid(s) in an amount that until step A2(v) is reached does not lead to any substantial independent precipitation quantities of silica particles having the tertiary aggregate structure of said Type-I, Type-II or Type-III to be subsequently precipitated out by step A2(v) sequentially added or

10 recycled or used sequentially from step A2(vi) in a quantity and of a size of particle where dissolved siliceous materials in said second geothermal fluid(s) accrete to said added particles but do not substantially precipitate out onto the internal surfaces of said apparatus (including any piping or channels) thereby at least reducing the amount of siliceous values adhering to said apparatus (including

15 any piping or channels) as well as enlarging said added particles and subsequently with step A2(vi) after the addition of at least one precipitation agent (which may comprise or include still additional quantities of silica particles of the desired tertiary aggregate structure, sequentially added or recycled or otherwise) recovering said grown added particles of tertiary aggregate amorphous silica of the

20 particular Type-I, Type-II or Type-III.

2. A process of claim 1 wherein part of said first portion of step A2(vi), whether as a slurry, gel or powder, is used sequentially or is recycled in a controlled amount to react with a newly separated geothermal water stream .

- 79 -

3. A process of claim 2 wherein said sequential or recycle reaction at least in part is between a first flashing and a second flashing and/or heat exchange of step A1.
- 5 4. A process of claim 2 or 3 wherein said sequential or recycle reaction at least in part is to the first flashing of step A1.
5. A process of any one of claims 1 to 4 wherein said amorphous silica is of Type-I.
- 10 6. A process of any one of claims 1 to 4 wherein the amorphous silica is of Type-II.
7. A process of any one of claims 1 to 4 wherein the amorphous silica is of
- 15 Type-III.
8. A process of any one of claims 1 to 4 wherein the amorphous silica is of Type I, Type II or Type III tertiary aggregate structure with an average secondary particle dimensions up to about 30 nm. and an oil absorption of greater than
- 20 about $190 \text{ g.}100\text{g}^{-1}$ as measured by the spatula rubout method using linseed oil, and a light scattering coefficient greater than about $280 \text{ m}^2.\text{kg}^{-1}$, and a reflectance of greater than about 95% at a wavelength of 557 nm.(using illuminant D65 and 10° viewing angle), and a BET surface area of greater than about $4 \text{ m}^2.\text{g}^{-1}$.

- 80 -

9. A process of any one of the preceding claims wherein said siliceous values in said source fluid comprises silicic acid.
10. A process of any one of the preceding claims wherein said source fluid
5 comprises silicic acid in a concentration of about 400 to 1,400 mg.kg⁻¹.
11. A process of any one of the preceding claims wherein said source fluid comprises said source fluid combined with a synthetic source of silicate ion or silicic acid which exceeds a concentration of about 400 mg.kg⁻¹.
- 10
12. A process as claimed in any one of the preceding claims wherein said apparatus is part of an electricity generating system and said steam drives directly or indirectly at least one turbine.
- 15 13. A process as claimed in any one of the preceding claims wherein step A1 includes a first flashing and either a second flashing or heat exchange and Type-I, Type-II or Type-III silica added by the improvement is at least added between said primary flashing and said secondary flashing or heat exchange.
- 20 14. A process as claimed in claim 13 wherein the second fluid with added substrate particles resulting from said secondary flashing or heat exchange is at a temperature of from 30°C to 100°C and has had a preformed silica addition thereto in a ratio from 0.1 - 50 g of preformed silica per kg of said geothermal fluid.

- 81 -

15. A process as claimed in claim 14 wherein said ratio is from 0.5 - 5g.
16. A process as claimed in any one of the preceding claims wherein said second fluid with added substrate particles is reacted to provide an oxygen free residence time of up to about 30 minutes.
17. A process as claimed in claim 16 wherein after said reaction time preferably in a precipitation reactor the fluid is conditioned preferably in a conditioner after flocculent addition which is the precipitation agent added with step A2(v).
18. A process as claimed in claim 16 or 17 wherein the reaction time preferably in the conditioner after flocculent addition is up to about 5 minutes.
19. A process as claimed in claim 17 or 18 wherein the fluid and/or precipitate from said conditioner is clarified preferably in a clarifier and the main silica carrying fraction thereof is separated from a lesser silica containing liquid fraction.
20. A process as claimed in claim 19 wherein the lesser silica containing fraction is subjected (optionally after further removal of particulate silica by filtering, settling or otherwise) to re-injection or alternative disposal.
21. A process as claimed in any one of the preceding claims wherein the silica product extracted from the main silica containing fraction or included therein has

- 82 -

a BET surface area of at least $4 \text{ m}^2.\text{g}^{-1}$.

22. A process as claimed in any one of claims 16 to 20 wherein at least part of the main silica containing liquid fraction is recirculated into a precipitation
5 reactor.

23. A process as claimed in any one of the preceding claims wherein Type-I, Type-II or Type-III silica is introduced between said primary flashing and said secondary flashing or heat exchange and is from an untreated source fluid, ie. is of
10 a type created by a process as claimed in a claim of New Zealand Patent Specification No. 232170/228472 which has not involved any reaction with any externally introduced silica particles.

24. A process of producing particles of amorphous silica having a tertiary
15 aggregate structure selected from at least one member of the group consisting of Type-I, Type-II or Type-III, which comprises:

providing a source fluid containing siliceous materials and an amount of a precipitation agent for said siliceous materials which is insufficient to cause substantial quantities of said siliceous materials to come out of solution in said
20 source fluid;

maintaining the pH of said fluid at up to about 9.5 during the following steps;

forming a silica sol, by causing said source fluid to become supersaturated with respect to amorphous silica and initiating polymerization of said siliceous

- 83 -

materials therein into polymeric material comprising primary particles of polymeric amorphous silica, without causing substantial quantities of said siliceous materials to be independently precipitated;

aging said silica sol, by holding such for a time sufficient to continue the polymerization of said siliceous materials in said sol into said polymeric material, without causing substantial quantities of said polymeric material to be independently precipitated;

adding to said silica sol a sufficient quantity of at least one of said precipitation agents to provide a sufficient proportion thereof, in relation to said polymeric material, to convert said polymeric material into silica particles having a tertiary aggregate structure of said Type-I, Type-II or Type-III, of an amount sufficient to cause rapid precipitation thereof from said silica sol;

thereby precipitating at least some of said tertiary aggregate amorphous silica particles to form a slurry of said particles;

harvesting at least a portion of said particles; and

sequentially adding or recycling at least a portion of said particles into admixture with said geothermal source fluid prior to said precipitation stage in an amount such that dissolved siliceous materials in said geothermal fluid are converted into primary particles and precipitate on to said sequentially added or recycled particles and cause them to grow to a larger effective secondary particle size.

25. A process as claimed in claim 24 including sequentially adding or recycling said particles as a slurry.

- 84 -

26. A process as claimed in claim 24 or 25 including sequentially adding or recycling said particles into admixture with said source fluid prior to supersaturation thereof with respect to amorphous silica.

5 27. A process as claimed in claim 24 wherein said source fluid is a geothermal source fluid.

28. A process as claimed in claim 24 including sequentially adding or recycling said particles into admixture with said source fluid prior to aging thereof.

10

29. A process as claimed in claim 24 including sequentially adding or recycling said particles into admixture with said source fluid after aging thereof.

30. A process as claimed in claim 24 whereby the admixture of geothermal
15 source fluid and tertiary aggregate Type I, II, or III silica which is to be harvested, is further treated with said precipitation agents to effect complete precipitation and yield effluent of low suspended solids.

31. A process as claimed in claim 24 whereby the admixture of geothermal
20 source fluid and tertiary aggregate Type I, II, or III silica which is to be harvested, is treated with equivalent solution concentrations of up to 5 mg.kg⁻¹ polyethylene oxide and up to 5 mg.kg⁻¹ of a high charge density polyamine, in order to effect complete precipitation and yield effluent of low suspended solids.

- 85 -

32. In a process of recovering energy from a hot, high pressure geothermal source fluid, containing dissolved siliceous values therein, derived from an underground source, which process comprises;

first flashing source fluid to a substantially lower pressure and temperature
5 to produce high pressure steam and to form a second fluid which is at a lower temperature and pressure and therefore has a higher effective concentration of siliceous values dissolved therein;

converting said high pressure steam to electricity;

and

10 recovering particles of tertiary aggregate amorphous silica from said second fluid by a process which comprises:

causing the relative amounts of said siliceous values and any precipitation agent contained in said second fluid to be insufficient to cause substantial quantities of said siliceous materials to come out of solution in said second fluid;

15 maintaining the pH of said second fluid at up to about 9.5 during the following steps;

forming a silica sol, by causing said second fluid to become supersaturated with respect to amorphous silica and initiating polymerization of said siliceous values therein into polymeric material comprising primary particles of polymeric
20 amorphous silica, without causing substantial quantities of said siliceous values, including polymers thereof, to independently precipitate;

aging said silica sol, by holding such for a time sufficient to continue the polymerization of said siliceous values in said sol into said polymeric material and into larger particles thereof, without causing substantial quantities of said

- 86 -

polymeric material or said particles to independently precipitate;

adding to said silica sol a sufficient quantity of at least one precipitation agent to provide a sufficient proportion thereof, in relation to said polymeric and particulate material, to convert said polymeric material and said particles into

5 silica particles having a tertiary aggregate structure of said Type-I, Type-II or Type-III, of a size sufficient to cause rapid precipitation thereof from said silica sol;

thereby precipitating at least some of said tertiary aggregate amorphous silica particles to form a slurry of said particles; and

10 separating said slurry into at least a first portion comprising said particles and a second portion comprising a more dilute aqueous medium;

the process to at least substantially reduce the amount of siliceous material which precipitates out of said geothermal source fluid on to internal surfaces of apparatus and piping used to carry out the process, which process comprises:

15 sequential addition or recycling a portion of said separated particles into admixture with said geothermal source fluid, in a proportion, taking into account the amount of siliceous values in said source fluid, sufficient to provide at least a critical coagulant concentration, prior to said flashing in an amount such that dissolved siliceous materials in said geothermal fluid accrete to said particles but
20 do not substantially precipitate out onto the internal surfaces of said apparatus and piping, thereby at least reducing the amount of siliceous values precipitated on and adhering to said apparatus, as well as enlarging said sequentially added or recycled particles of tertiary aggregate amorphous silica; and

recovering at least a portion of said enlarged particles of tertiary aggregate

- 87 -

amorphous silica.

33. A process as claimed in claim 32 including subjecting said geothermal source fluid to a first, high pressure flashing to produce high pressure steam and a first aqueous liquid underflow at lower elevated pressure and temperature than said source fluid which contains said siliceous values; subjecting said underflow to a second, lower pressure flashing to produce lower pressure steam and a second aqueous liquid underflow; converting said steam to electricity; recovering siliceous values from said second underflow; and sequentially adding or recycling a portion of said particulate product, in slurry form, into admixture with said first underflow.

34. A process as claimed in claim 32 including subjecting said geothermal source fluid to a first, high pressure flashing to produce high pressure steam and a first aqueous liquid underflow at lower elevated pressure and temperature than said source fluid which contains said siliceous values; subjecting said underflow to a second, lower pressure flashing to produce lower pressure steam and a second aqueous liquid underflow; converting said steam to electricity; recovering siliceous values from said second underflow; and sequentially adding or recycling a portion of said particulate product, in slurry form, to said high pressure flashing.

20

35. A process as claimed in claim 32 wherein said steam from said first flashing drives a high pressure, electricity generating turbine which produces a spent stream, comprising lower pressure and temperature steam; and driving a second, lower pressure, electricity generating turbine with both said spent stream and said

- 88 -

steam from said second flashing.

36. A process as claimed in claim 32 including reinjecting said more dilute aqueous medium into the underground source of said geothermal source fluid.

5

37. A process as claimed in claim 32 wherein said source fluid contains minerals in addition to siliceous values, and including the further step of, after recovering said particulate silica and forming said more dilute aqueous medium, recovering at least a portion of said additional minerals from said more dilute

10 aqueous medium.

38. A process as claimed in claims 32 wherein said geothermal source fluid contains arsenic values, and wherein said improved process produces a particulate amorphous silica product which contains less arsenic than would particulate silica

15 recovered from said source fluid without said sequential addition or recycle.

39. The product(s) of any one of the preceding claims.

40. Paper containing a product claimed in claim 39 therein in admixture with

20 the fibres thereof.

41. Paper having the product claimed in claim 39 disposed on the surface thereof.

- 89 -

42. A silica product having tertiary aggregate structure with an average secondary particle dimensions up to about 30 nm. and an oil absorption of greater than about 190 g.100g⁻¹ as measured by the spatula rubout method using linseed oil, and a light scattering coefficient greater than about 280 m².kg⁻¹, and a reflectance of greater than about 95% at a wavelength of 557 nm.(using iluminant D65 and 10° viewing angle), and a BET surface area of greater than about 4 m².g⁻¹.
43. A silica product obtained from geothermal water having a tertiary aggregate structure with an average secondary particle dimensions up to about 30 nm. and an oil absorption of greater than about 190 g.100g⁻¹ as measured by the spatula rubout method using linseed oil, and a light scattering coefficient greater than about 280 m².kg⁻¹, and a reflectance of greater than about 95% at a wavelength of 557 nm.(using iluminant D65 and 10° viewing angle), and a BET surface area of greater than about 4 m².g⁻¹.
44. A silica product having a Type I, II or III tertiary aggregate structure with an average secondary particle dimensions up to about 30 nm. and an oil absorption of greater than about 190 g.100g⁻¹ as measured by the spatula rubout method using linseed oil, and a light scattering coefficient greater than about 280 m².kg⁻¹, and a reflectance of greater than about 95% at a wavelength of 557 nm.(using iluminant D65 and 10° viewing angle), and a BET surface area of greater than about 4 m².g⁻¹.

- 90 -

45. A silica product obtained from geothermal water having a Type I, Type II or Type III tertiary aggregate structure with an average secondary particle dimensions up to about 30 nm. and an oil absorption of greater than about 190 g.100g⁻¹ as measured by the spatula rubout method using linseed oil, and a light scattering coefficient greater than about 280 m².kg⁻¹, and a reflectance of greater than about 95% at a wavelength of 557 nm.(using illuminant D65 and 10° viewing angle), and a BET surface area of greater than about 4 m².g⁻¹.
- 10 46. The use of a silica product in paper whereby paper filled with the silica product has an increased opacity by at least 1 point, an increase in brightness of at least 1 point and a reduction in the printed opacity of at least 15% for each one % weight/weight addition of Type I silica, compared with paper prepared from the same pulp furnish and made under the same conditions but without the addition of Type I silica.
- 15 47. A silica product which when added in an amount up to about 30 kg/tonne to newsprint of basis weight of about 35 gsm or greater results in an increased opacity by at least 1 point, an increase in brightness of at least 1 point and a reduction in the printed opacity of at least 15% for each one % weight/weight addition of silica, compared with paper prepared from the same pulp furnish and made under the same conditions but without the addition of silica.
- 20

- 91 -

48. A composite particle which has a core of another material, such as clay, calcium carbonate etc, around which or onto which a coating of silica is deposited by the process of recovering silica from geothermal water as claimed in anyone of claims 1 to 38.
- 5
49. Paper coated with a coating formulation and/or impregnated with a formulation which has as one of its components Type I,II or III silica made by a process as claimed in any one of claims 1 to 38.
- 10 50. Cement or cementitious products, including concrete to which Type I, Type II or Type III silica made by a process of any one of claims 1 to 38, has been added as one of the components of the mix.
- 15 51. Paint with a formulation which has as one of its components Type I,II or III silica made by a process of any one of claims 1 to 38.
52. Rubber having as a one of its components Type I,II or III silica made by a process of any one of claims 1 to 38.
- 20 53. A filler composition having as its principal active component Type I,II or III silica made by a process of any one of claims 1 to 38.
54. A substantially inert extender composition having as its principal active component Type I,II or III silica made by a process of any one of claims 1

- 92 -

to 38.

55. A thixotropic agent having as its principal active component Type I,II or III silica made by a process of any one of claims 1 to 38.
- 5
56. An opacifier composition having as its principal active component Type I,II or III silica made by a process of any one of claims 1 to 38.
57. An absorbent comprising Type I,II or III silica made by a process of any one of claims 1 to 38.
- 10
58. An adhesive composition having as its principal active component Type I,II or III silica made by a process of any one of claims 1 to 38.
- 15 59. A method of applying an agricultural chemical to land which comprises absorbing said agricultural chemical onto the surface of particles of Type I,II or III silica made by a process of any one of claims 1 to 38
60. An anticaking agent having as its principal active component Type I,II or III silica made by a process of any one of claims 1 to 38.
- 20
61. A battery separator having as its principal active component Type I,II or III silica made by a process of any one of claims 1 to 38.

- 93 -

62. Toothpaste having as one of its active components Type I,II or III silica made by a process of any one of claims 1 to 38.
63. A ceramic composition or formulation having as one of its components
5 Type I,II or III silica made by a process of any one of claims 1 to 38.
64. A mineral recovery process which utilises as its feed stock geothermal water from which the dissolved silica has been recovered substantially or in part, by a process of any one of claims 1 to 38.
- 10
65. A process as claimed in claim 32 wherein the dissolved silica in geothermal water is removed substantially or in part thereby forming a more dilute aqueous solution and thereafter providing said more dilute aqueous solution to a further process for the removal in part or otherwise of other
15 dissolved minerals or components in said solution.
66. The use of a silica product in paper whereby paper filled with the silica product has an increased opacity by at least 1 point, an increase in brightness of at least 1 point and a reduction in the printed opacity of at
20 least 15% for each one % weight/weight addition of silica, compared with paper prepared from the same pulp furnish and made under the same conditions but without the addition of silica.

1/18

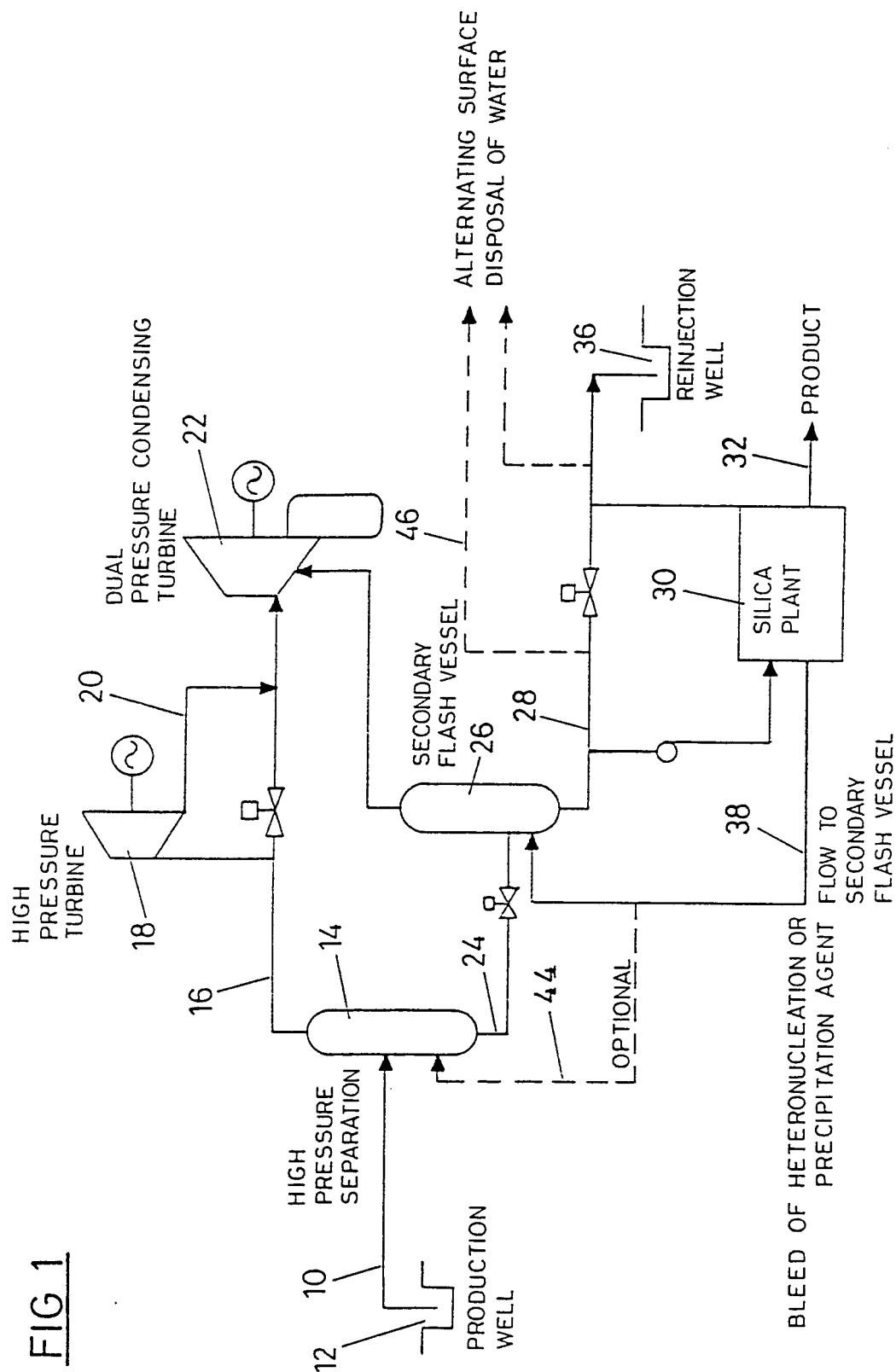


FIG 2

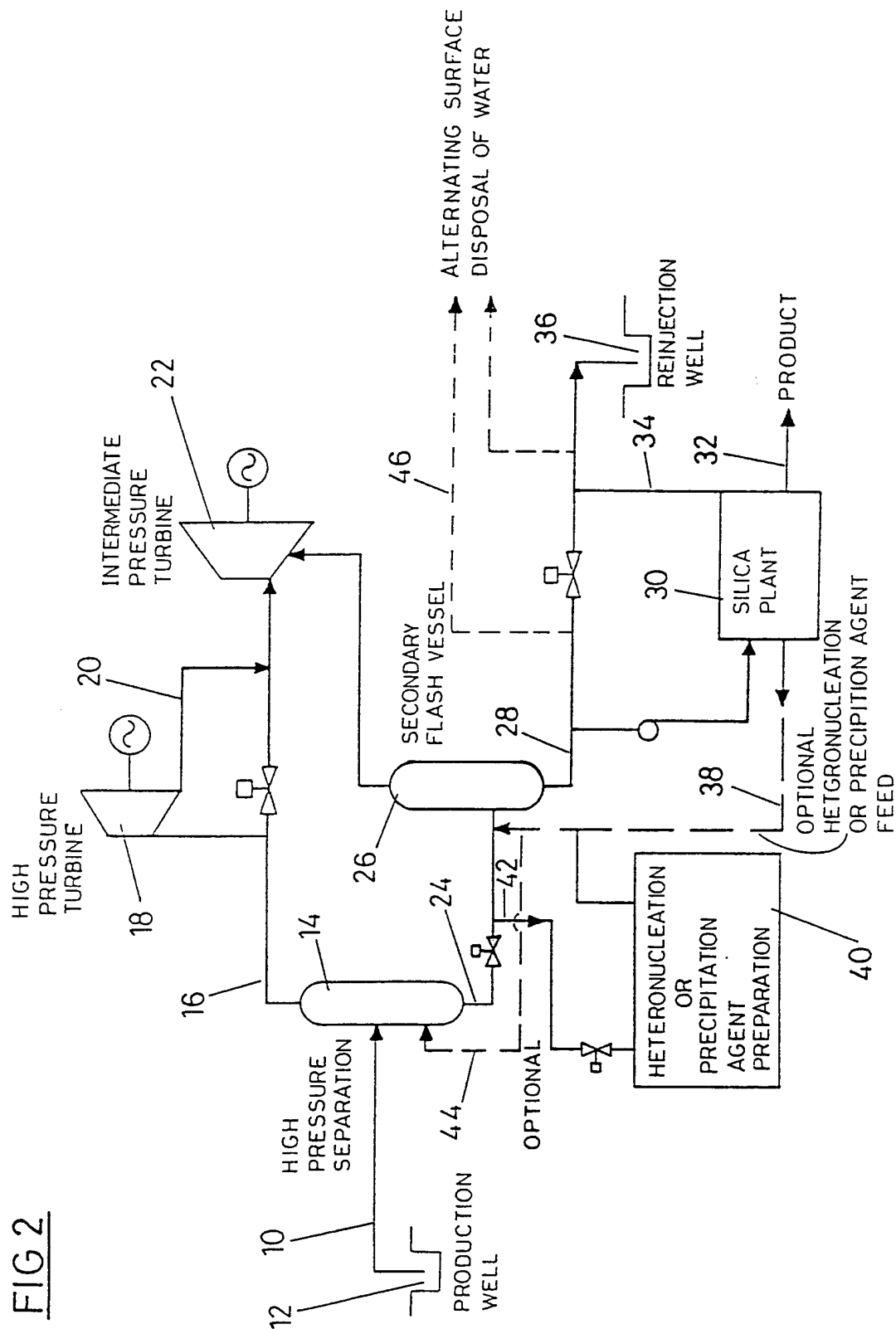
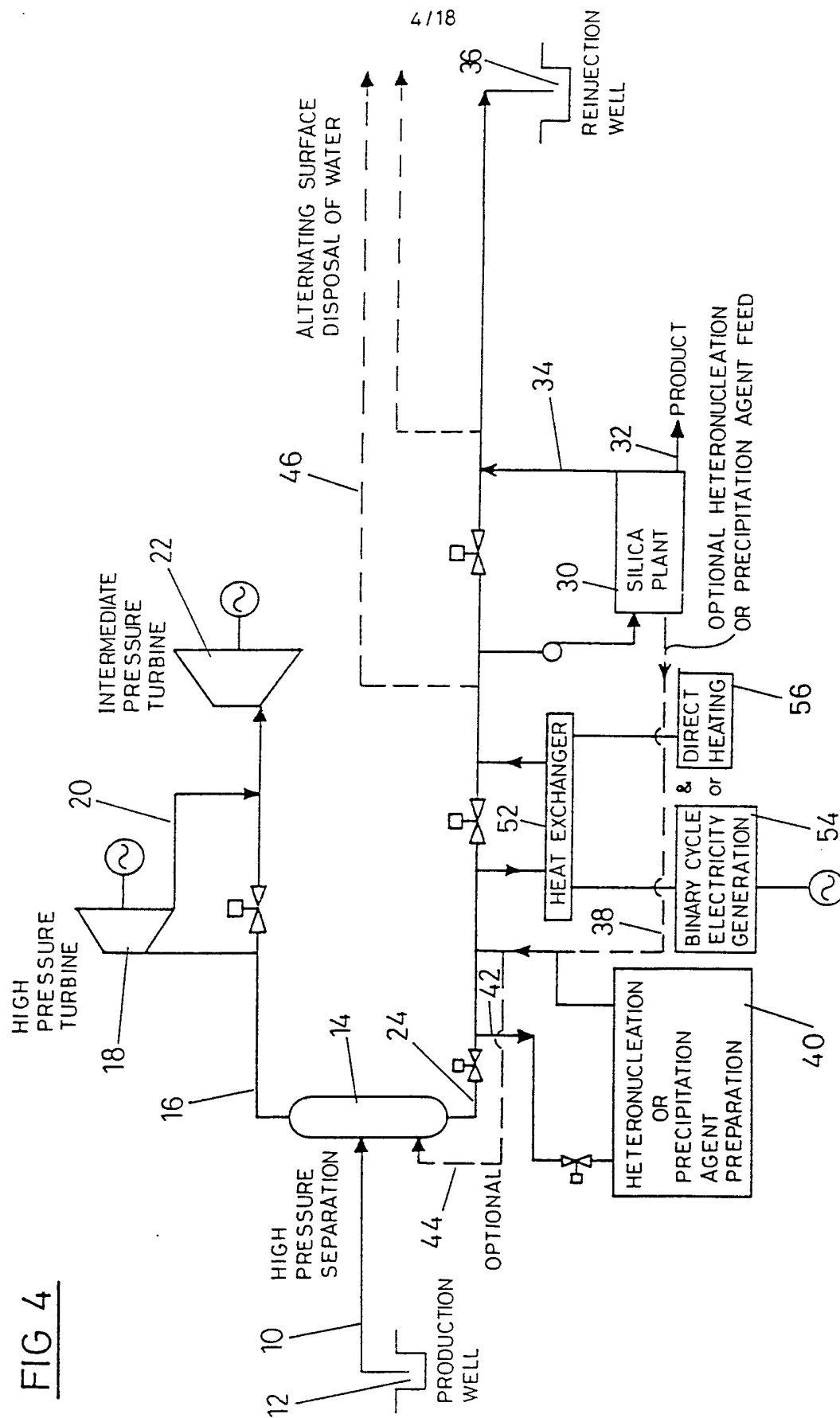


FIG 4



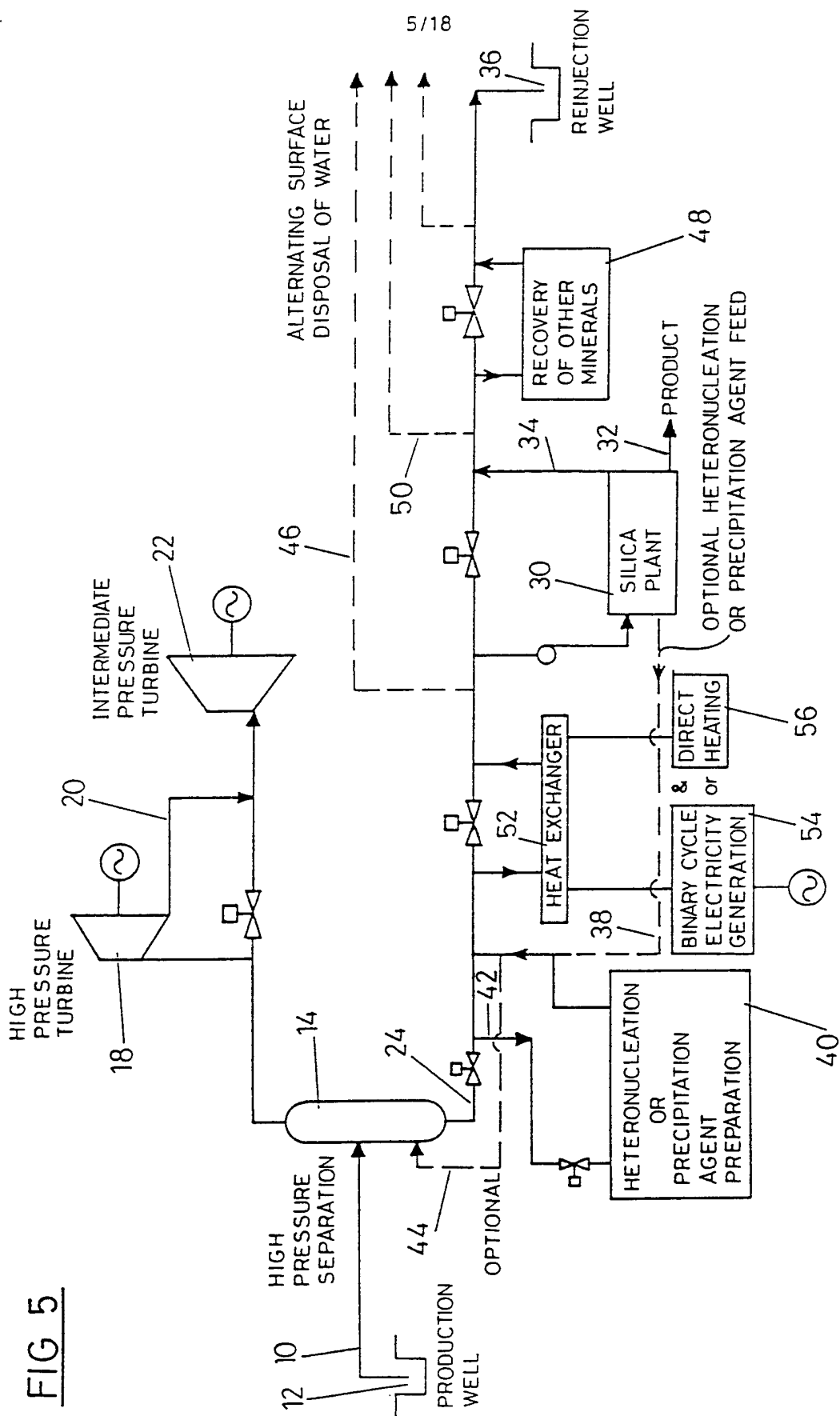
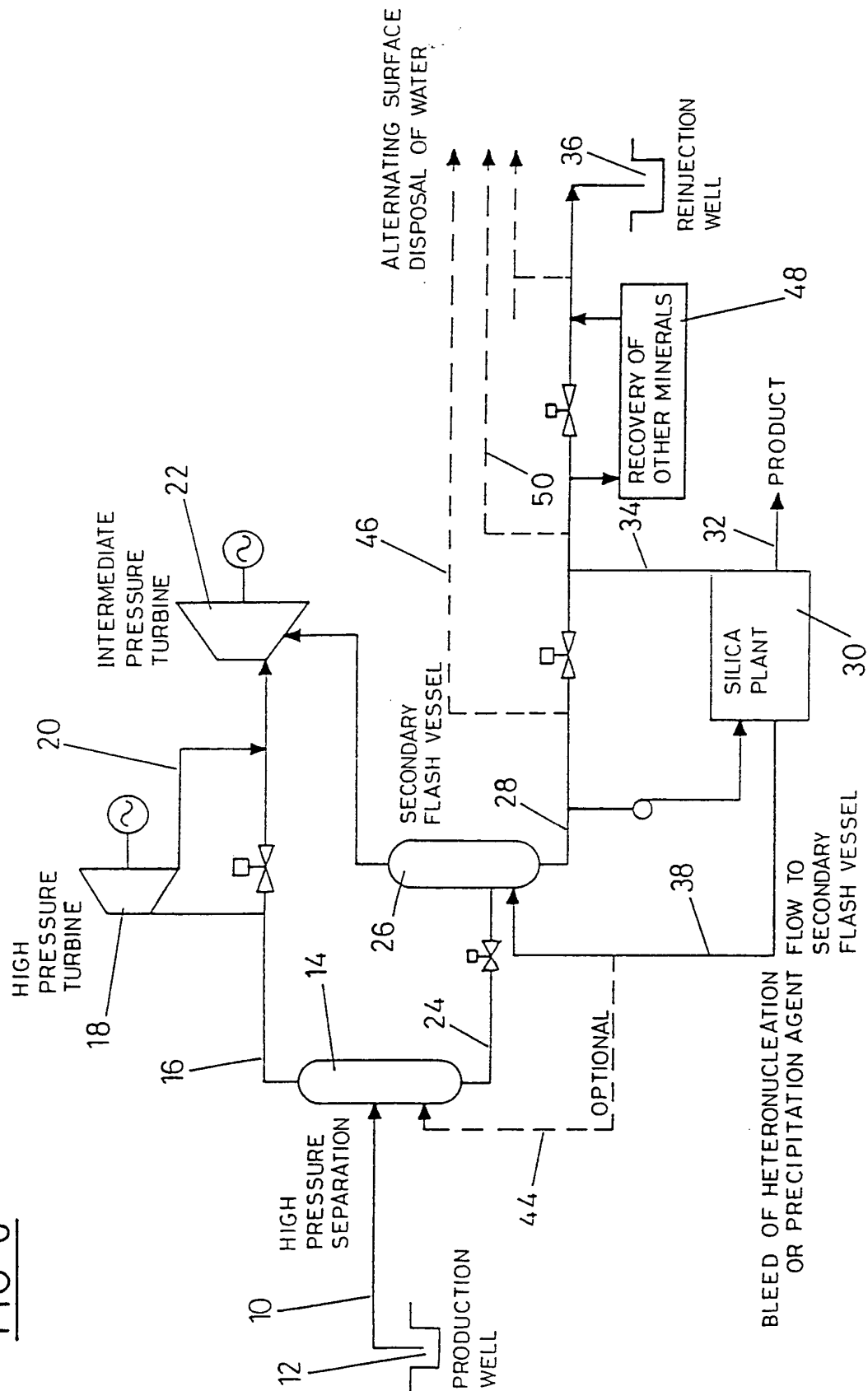


FIG 6



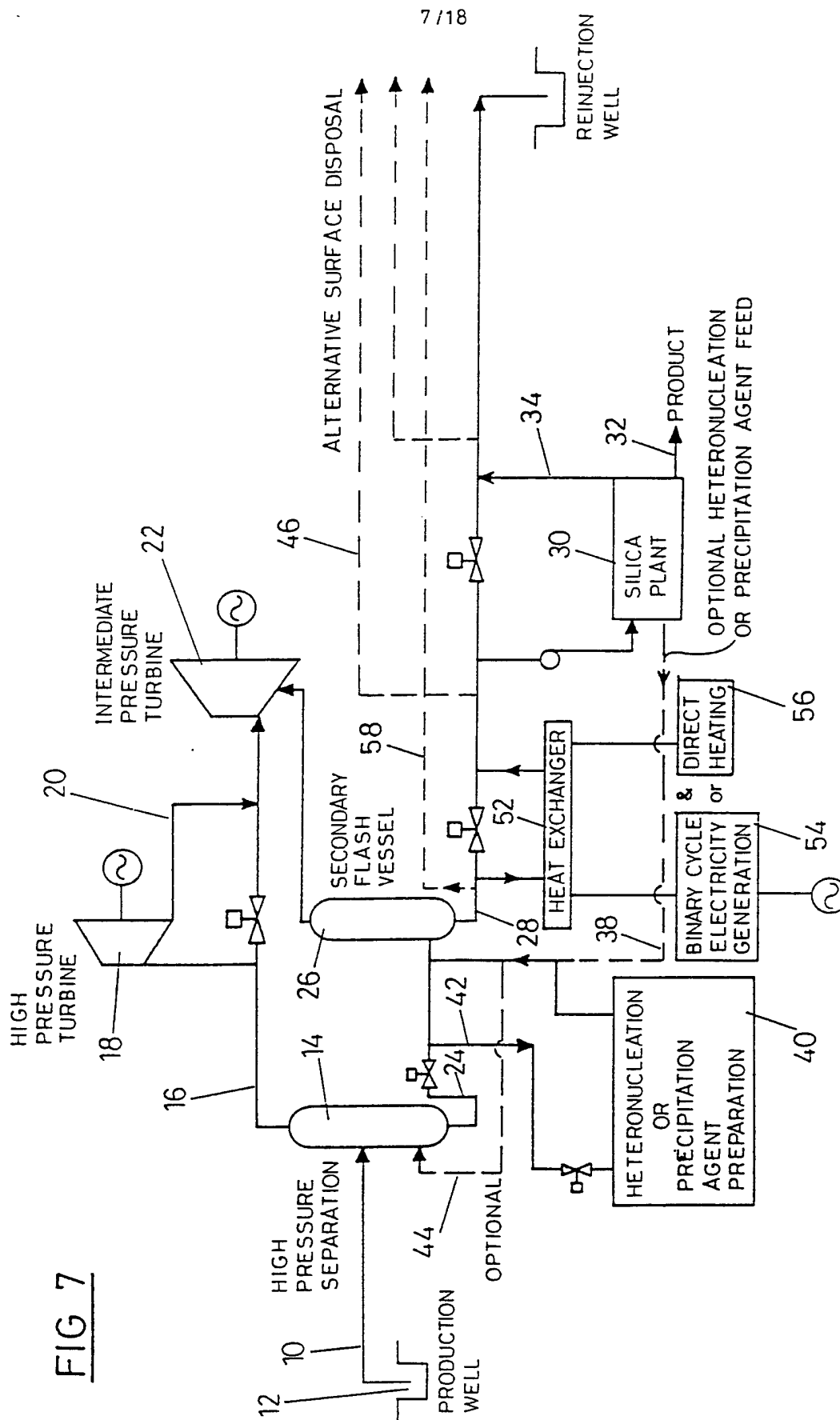
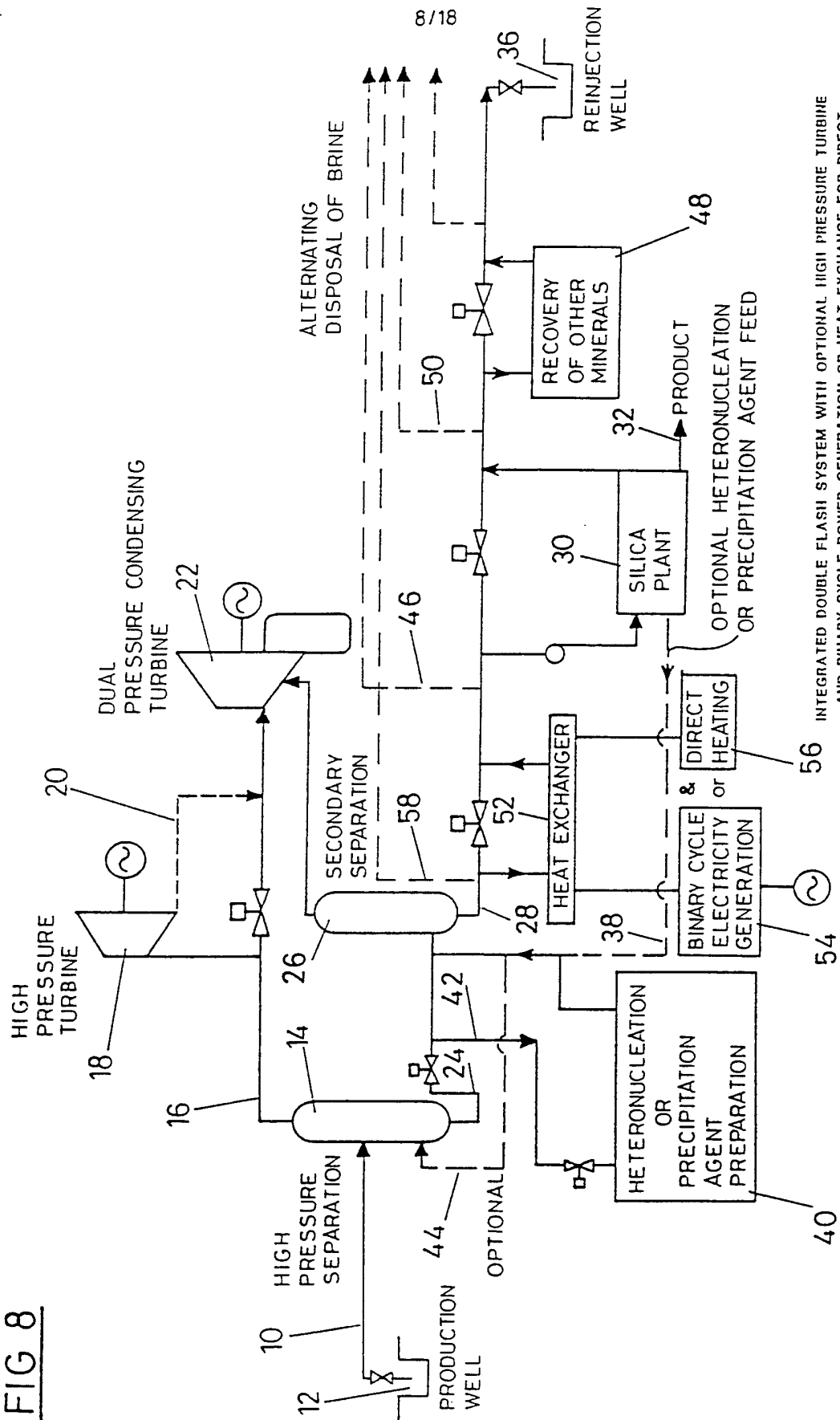


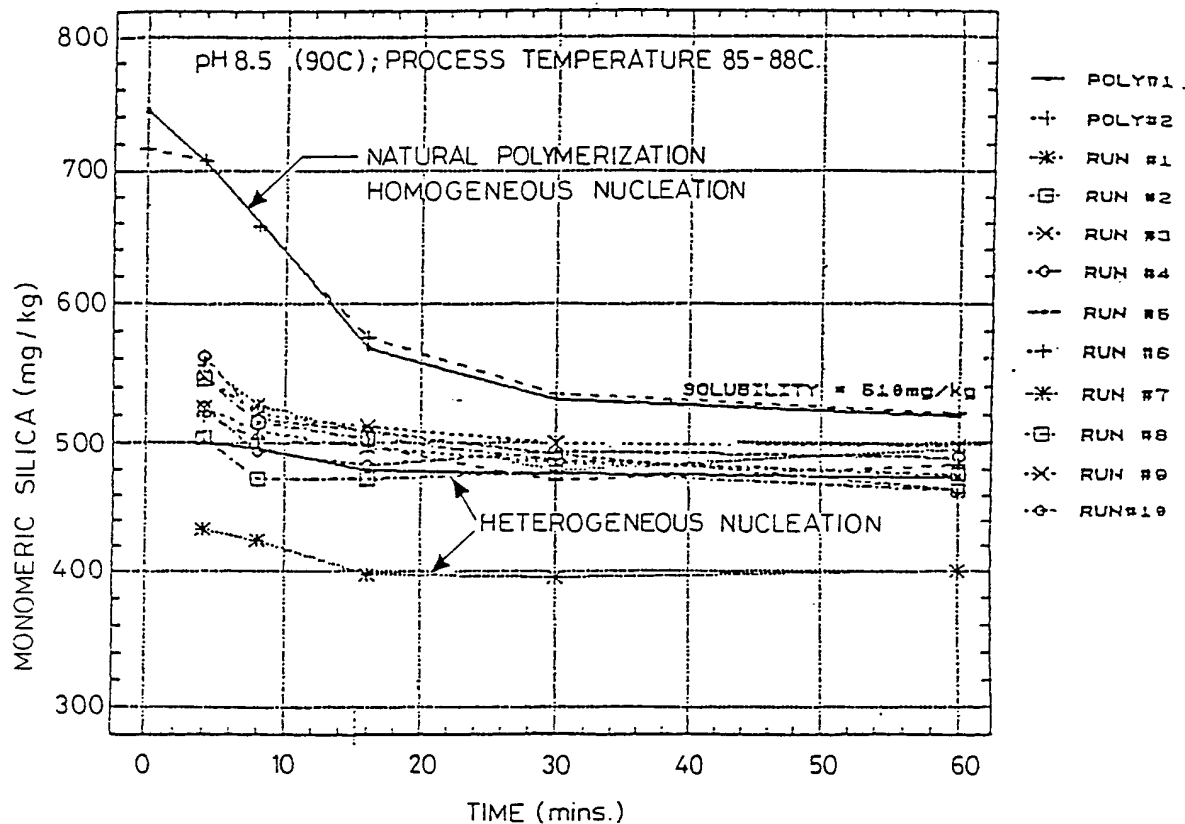
FIG 7

FIG 8



9/18

POLYMERIC SILICA REMOVAL; KAWERAU WATER
MONOMERIC SILICA VS. TIME; PROCESS WATER



Legend:

1. Poly #1 and #2 are polymerization curves for Kaueru geothermal water. Polymerization has proceeded naturally upon aging at constant temperature and pH.
2. In runs #1 - #10, freshly supersaturated geothermal water is mixed with Type I silica. Within 4 minutes, the monomer silica concentration decreased to close to that at equilibrium. A reduced equilibrium solubility is established at 60 minutes,

FIG 9

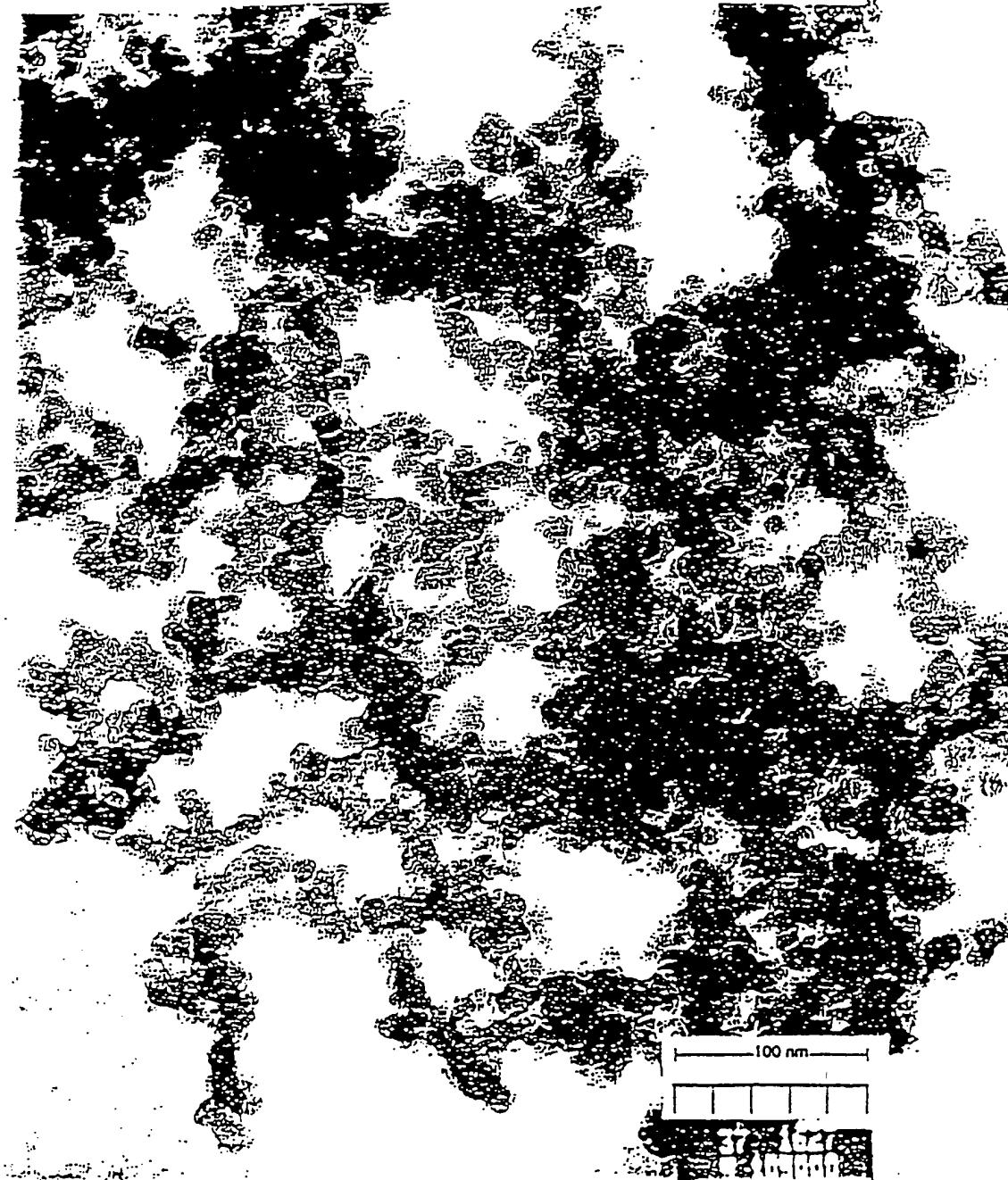
10/18



FIG 10

11/18

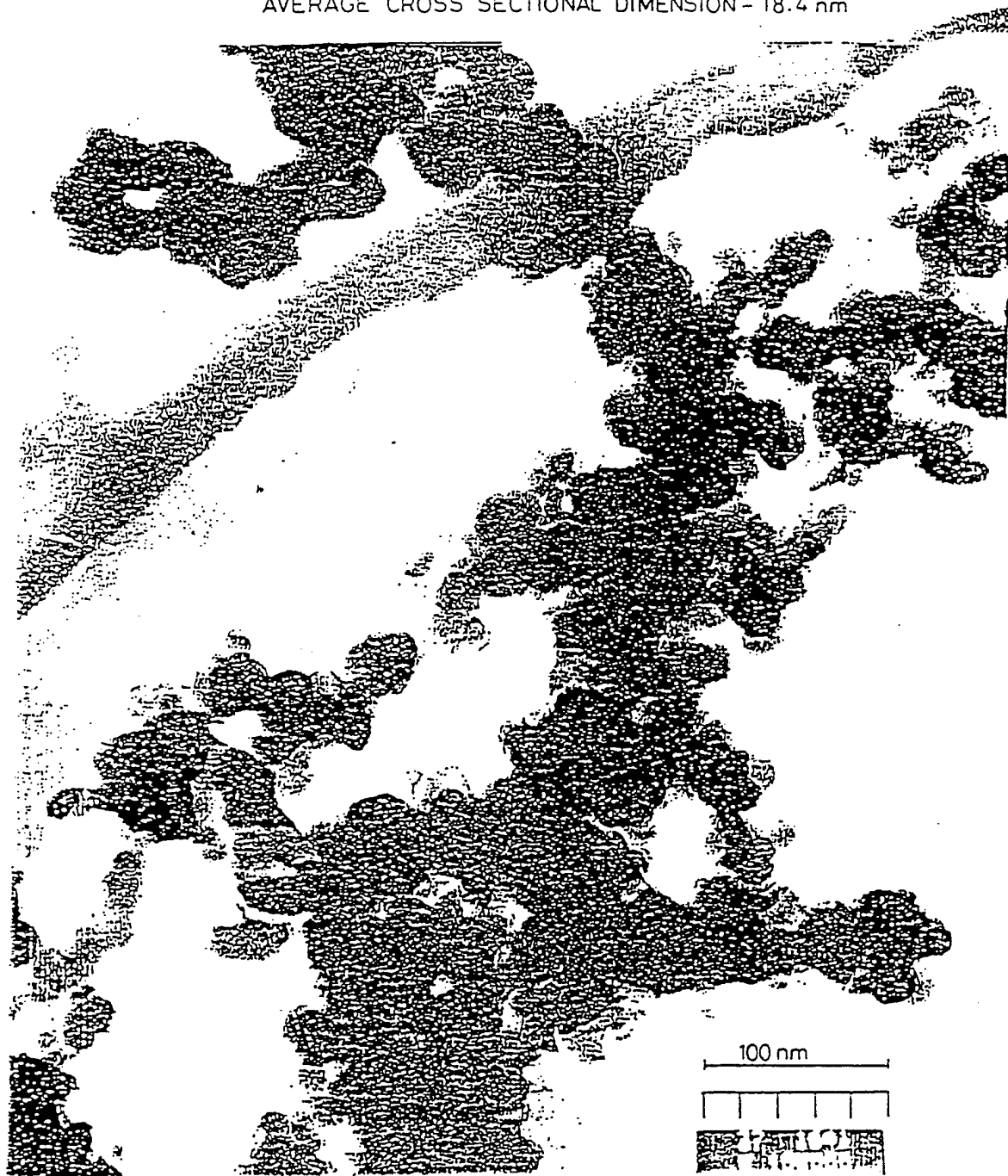
TYPE I SILICA - AFTER 5 RECYCLES
AVERAGE CROSS SECTIONAL DIMENSION - 11.7 nm.

FIG 11

12/18

TYPE 1 SILICA - AFTER 10 RECYCLES

AVERAGE CROSS SECTIONAL DIMENSION - 18.4 nm

FIG 12

TYPE 1 SILICA - AFTER 15 RECYCLES
AVERAGE CROSS SECTIONAL DIMENSION - 25.8 nm

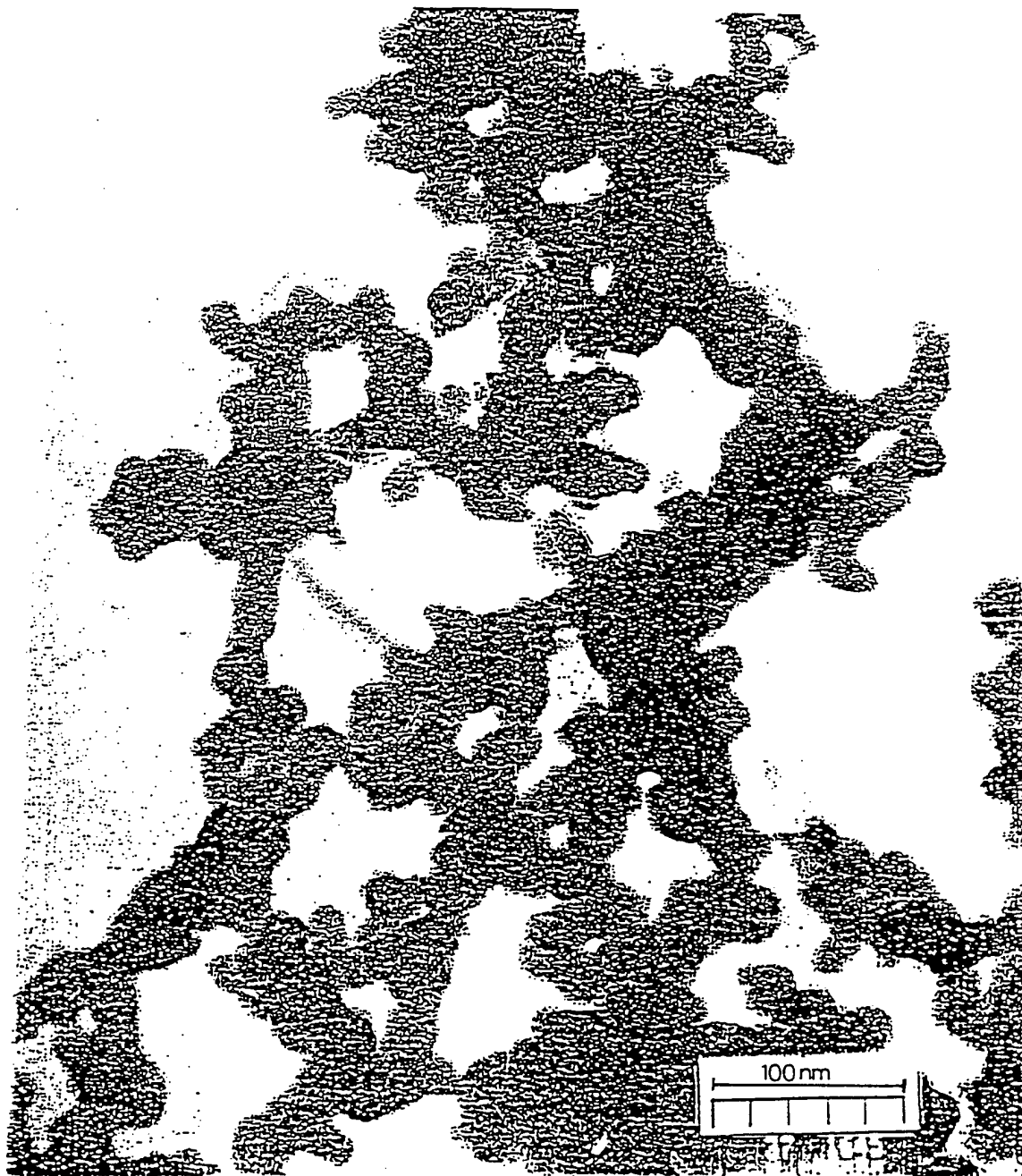


FIG 13

TYPE 1 SILICA - AFTER 20 RECYCLES
AVERAGE CROSS SECTIONAL DIMENSION - 28.7 nm

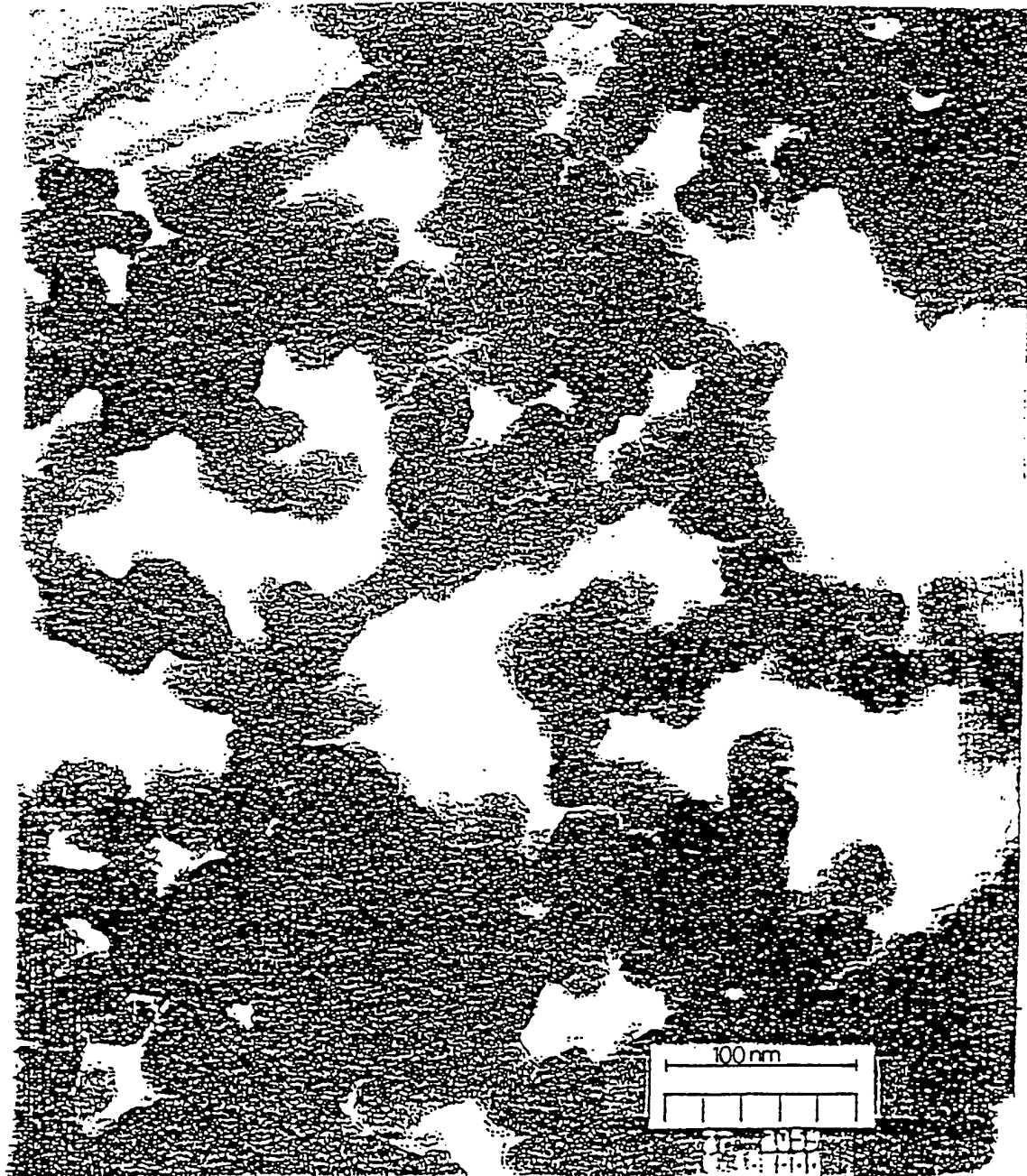


FIG 14

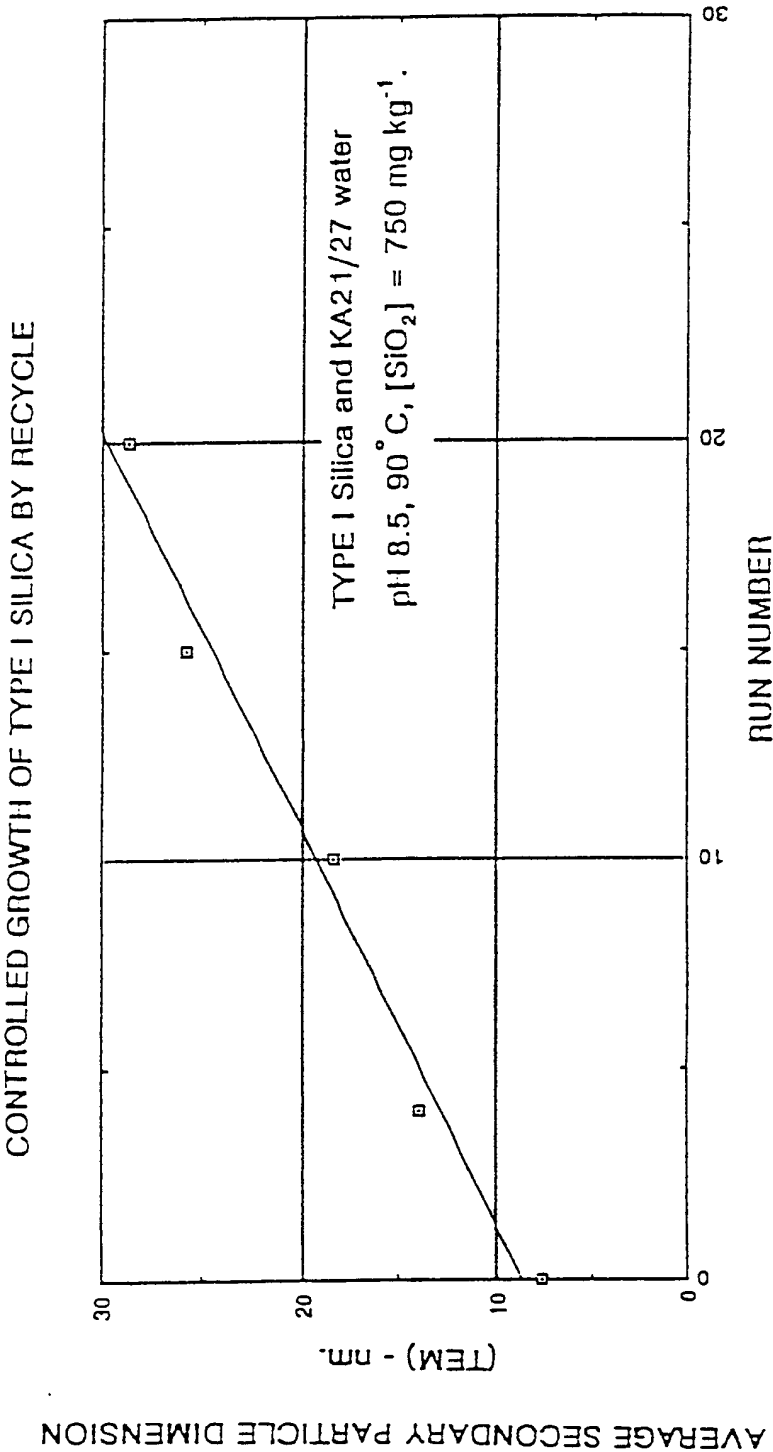
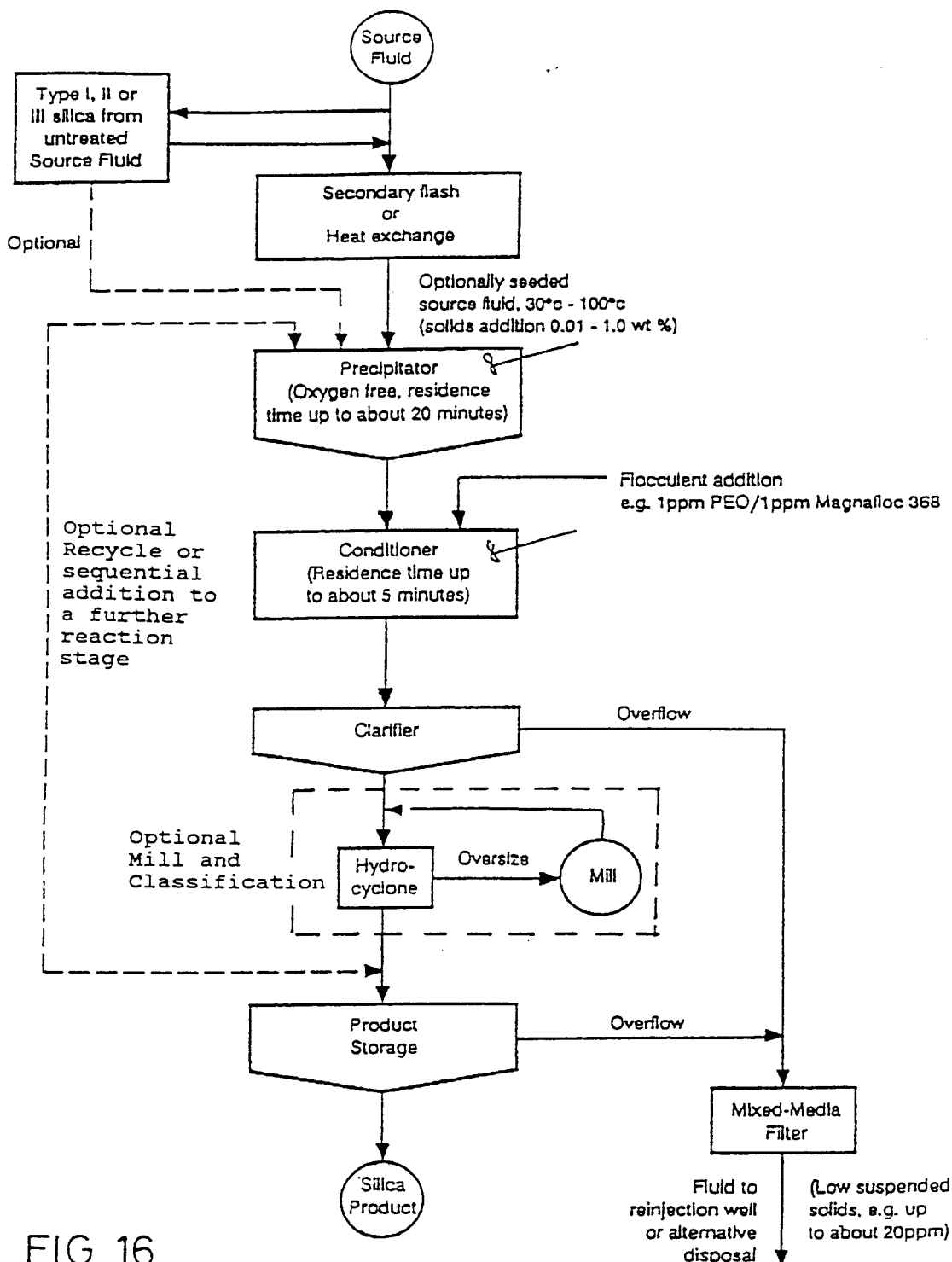


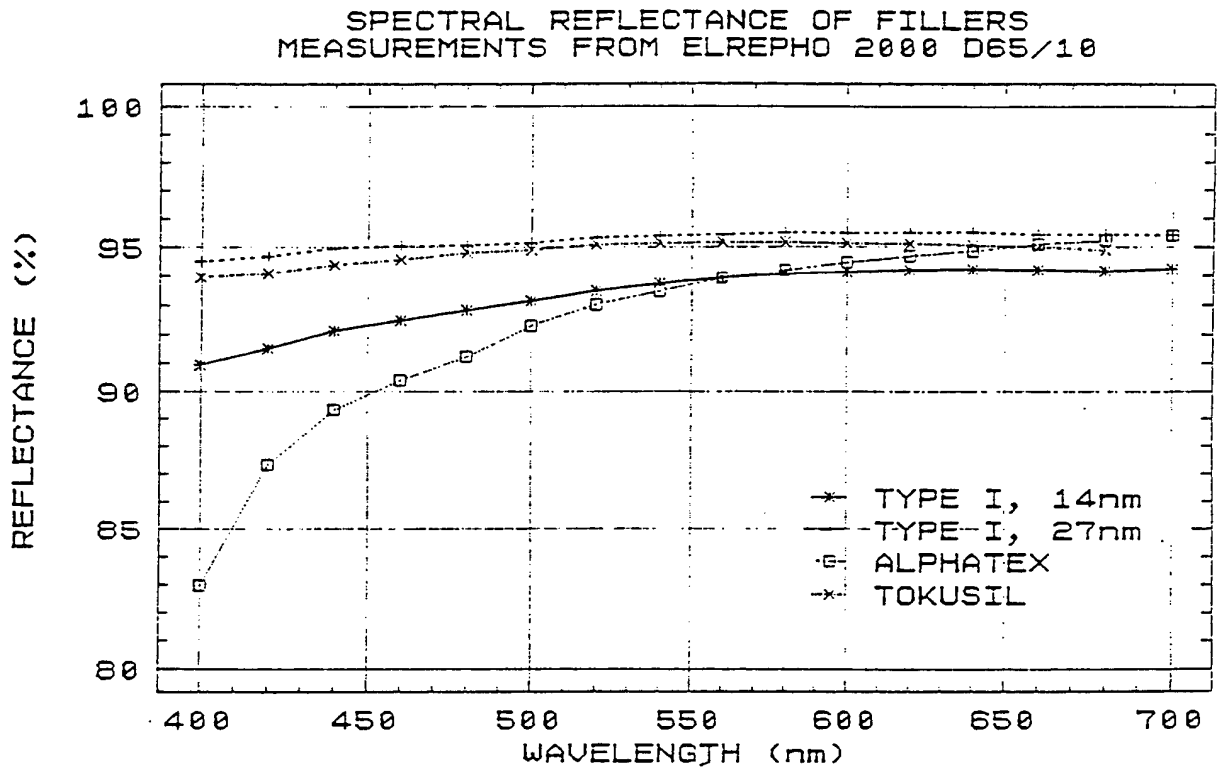
FIG 15

16/18



Schematic Diagram of Continuous Process
with Provision for Recycle

17/18

FIG 17a

Spectral Reflectance of Fillers

As measured using the Elrepho 2000

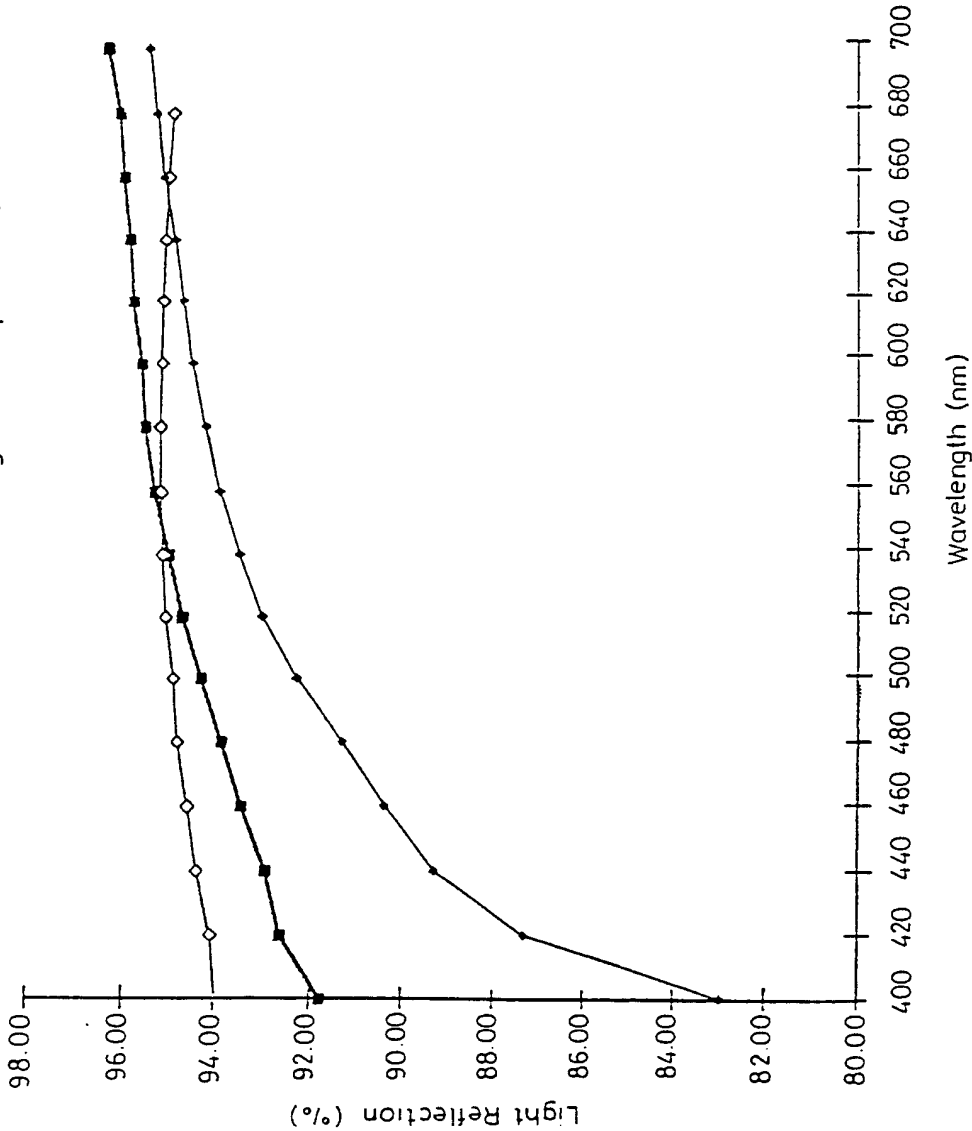
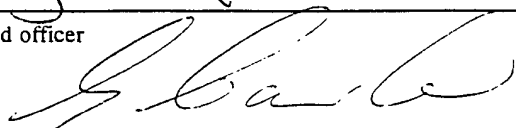


FIG 17b

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ C01B 33/12, D21H 17/68 According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC C01B 33/12, D21H 17/68 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT : Geotherm and (Si or silica or SiO ₂) JAPIO : Geotherm and (Si or silica or SiO ₂)					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.			
A	US,A, 4429535 (FEATHERSTONE) 7 February 1984 (07.02.84)				
A	EP,A, 396242 (TASMAN PULP & PAPER) 7 November 1990 (07.11.90)				
A	Patent Abstracts of Japan, C-466, page 16, JP,A, 62-158111 (NIPPON STEEL CORP) 14 July 1987 (14.07.87)				
A	Patent Abstracts of Japan, C-208, page 142, JP,A, 58-190816 (SHOKUBAI KASEI KOGYO K.K.) 7 November 1983 (07.11.83)				
	(continued)				
<div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div> <input checked="" type="checkbox"/> See patent family annex. </div> </div>					
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 10%; vertical-align: top; text-align: center;"> "T" "X" "Y" "&" </td> <td style="width: 40%; vertical-align: top;"> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family </td> </tr> </table>			* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family			
Date of the actual completion of the international search 2 May 1994 (02.05.94)		Date of mailing of the international search report 5 May 1994 (05.05.94)			
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929		Authorized officer  G. CARTER Telephone No. (06) 2832154			

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	GB,A, 819361 (FARBENFABRIKEN BAYER A.G.) 2 September 1959 (02.09.59)	
A	US,A, 2943971 (L.B. TAYLOR) 5 July 1960 (05.07.60)	

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international search report has not established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1-46 are directed to silica and a process of recovering silica from geothermal fluids whereas claims 46,47,66 are directed to silica having particular properties related to the addition of silica to paper.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	396242	AU	52136/90	CA	2012954	EP	396242
		FI	901416	JP	3033009	NO	901324
		NZ	228472	US	5200165	NZ	232170
END OF ANNEX							